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STABILITY OF COLLOIDAL GOLD UNDER HYDROTHERMAL CONDITIONS.

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ABSTRACT.

Colloidal silica protects colloidal gold both against electrolyte and against spontaneous coagulation by increase of temperature. The stability of unprotected and, in particular, protected sols toward electrolyte increases with increasing temperature. Unprotected sols containing no added electrolyte coagulate spontaneously at 150° to 250° C., but protected sols are stable at 350° C. The stability of protected and unprotected negative gold sols toward electrolyte is increased by the addition of NaOH, within a certain limit, but is decreased by the addition of HCl. The conditions of transportation and deposition of gold in acid and alkaline hydrothermal solutions are discussed.

Silica exists as a colloid in water at 25° and 100°, and probably at 350°, in dilutions considerably under the true solubilities reported by Hitchen and by Gruner. Their values may represent a colloidal peptization equilibrium that simulates a solubility curve.

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INTRODUCTION.

THE state in which gold is present in hydrothermal solutions has been recently discussed by Lindgren,[1] who reached the tentative conclusion that under alkaline conditions gold can exist only as a sol, protected by colloidal silica. However, information is lacking on the stability and behavior of gold sols at elevated temperatures. In addition, the experimental data on the effect of colloidal silica on colloidal gold are scant and are not in agreement as to the existence of a protecting action.

In the present paper are summarized the results of an exploratory experimental investigation directed primarily at: (1) the effect of temperature on the resistance toward electrolyte of unprotected and protected gold sols, (2) the spontaneous coagulation of electrolyte-free unprotected and protected gold sols with increase of temperature, (3) the effect of NaOH and HCl on the stability of unprotected and protected gold sols, and (4) the protecting action of silica itself. The geological implications of the data are discussed, with particular reference to the factors influencing the formation and coagulation of colloidal gold in natural hydrothermal solutions.

PREPARATION.

The recipes for the gold and silica sols used in the study are given below. The gold sols were reduced by H_2O_2 to avoid organic reducing agents. The H_2O_2 preparation used should, therefore, not contain acetanilid or other organic stabilizer.

Sol A (Au): 500 cc. of H_2O containing 1 cc. of 1 per cent auric chloride ($AuCl_3.HCl.3H_2O$) and 0.5 cc. of 0.1 N K_2CO_3 was brought to 85° C. and 1 cc. of 0.5 per cent H_2O_2 added dropwise with constant stirring. A blue sol is formed at first, due to partial reduction of the auric chloride to hydrous aurous oxide, which then changes to red (metallic gold) in a minute or so. The sol was then brought to boiling and a cold solution of 1 cc. of 1 per cent auric chloride, 0.5 cc. of 0.1 N K_2CO_3 and 1 cc. of 0.5 per cent H_2O_2 in 100 cc. of water was slowly stirred in. The sol was boiled for 20 minutes. The sol is deep red in color by transmitted light, with a faint brown cloudiness in reflected light. The sol was not dialyzed. Stock solutions of two or more liters were prepared in 600 cc. portions. No change in color or in coagulation value of the sol was observed after standing seven weeks.

[1] Lindgren, W.: Am. Inst. Min. Met. Eng., Tech. Pub. 713, p. 16, 1936.

Sols A1, A2 and A4 (Au): Prepared by dilution of sol A with 1, 2 and 4 volumes of water, respectively.

Sol B (Au): Prepared as in A, but 1 cc. of 0.1 N K_2CO_3 used.

Sols B1 and B2 (Au): Prepared by dilution of sol B with 1 and 2 volumes of water, respectively.

Sol C (Au): Prepared as in A, but reduced at 70°. The sol was then boiled for a few minutes. This sol developed a violet tint of color after standing about ten days, and experiments with it were then discontinued.

Sols C2 and C4 (Au): Prepared by dilution of sol C with 2 and 4 volumes of water, respectively.

Sol D (Au): 500 cc. of H_2O containing 2 cc. of 1 per cent auric chloride and 1 cc. of 0.1 N K_2CO_3 was reduced at 90° by the dropwise addition of 1.5 cc. of 0.5 per cent H_2O_2 and then boiled for 20 minutes. The sol was deep garnet red by transmitted light and tawny brown by reflected light. This sol is not readily reproducible.

Sol E (Au_2O): A hydrous aurous oxide sol was prepared by reducing 1 cc. of 1 per cent auric chloride plus 1.5 cc. of 0.1 N K_2CO_3 in 500 cc. of H_2O by the addition of 1 cc. of 0.5 per cent H_2O_2. The sol was boiled for 30 minutes. This sol is a clear deep blue, and corresponds to the blue stage of sol formation noted in the preceding preparations.

Sol F (SiO_2): A silica sol was prepared by adding sodium silicate to an amount of HCl insufficient to cause gelatinization. The sol was then diluted and electrodialyzed, beginning with a low current density, until chloride-free and for 60 hours thereafter. The sol was analyzed and diluted to 2.00 g. SiO_2 per liter.

Sol G (SiO_2): Silica gel was precipitated from sodium silicate by HCl, washed, and peptized in water by the addition of sufficient NaOH. The sol was then diluted and electrodialyzed for seven days. The sol was analyzed and diluted to 0.54 g. SiO_2 per liter.

Sol H (SiO_2): Prepared as above. Analyzed and diluted to 1.55 g. SiO_2 per liter. This sol and the preceding silica sols became perceptibly turbid after standing 3 to 5 weeks and deposited a very slight, flocculent precipitate, due to an increase in size and agglomeration (ageing) of the sol particles.

EXPERIMENTS.

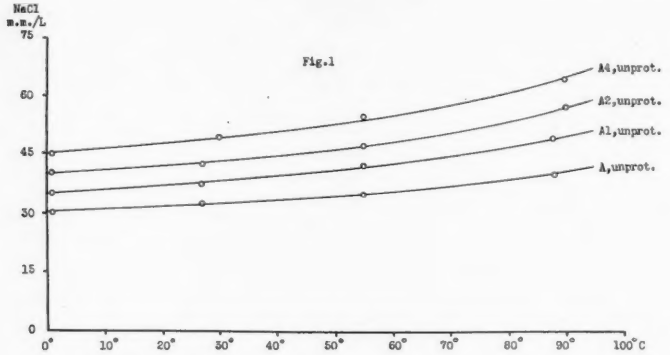
Effect of Temperature on the Coagulation Values of Unprotected Gold Sols.

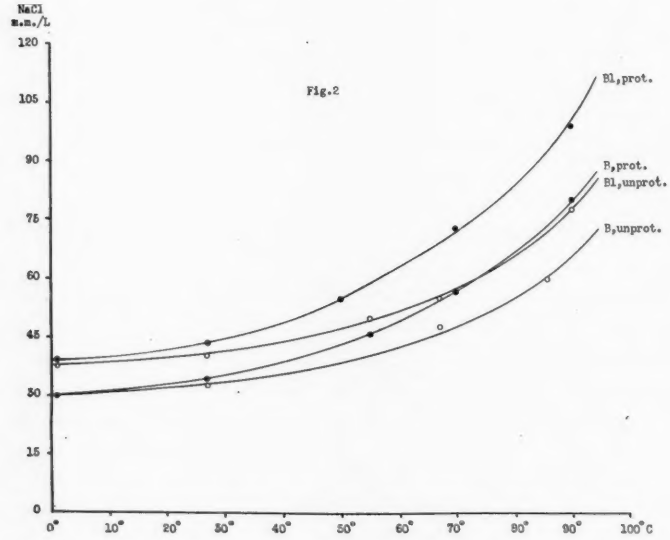
The measured change with temperature of the amount of NaCl necessary to effect coagulation of the unprotected sols in various dilutions is represented in Figs. 1–4. In every case, increase of temperature increases the stability toward electrolyte. The rate of increase differs for different sols, and, within the range of measurement, accelerates with increasing temperature.

An increase of stability is also effected by dilution of the gold sol. The opposite behavior has been found for a gold sol prepared by the formaldehyde method.[2] From the data of sols A,

[2] Ghosh, S., and Dhar, N. R.: Jour. Phys. Chem., **vol. 31, p. 187, 1927.**

A1, A2 and A4, the rate of increase of coagulation value with dilution is not linear, but drops off at high dilutions. The rate of change of coagulation value with temperature remains about the same with dilution. The effect of dilution in increasing the





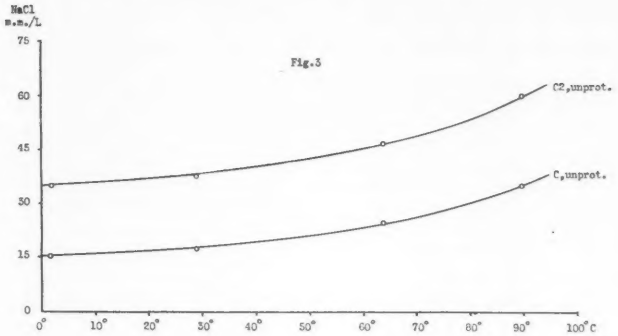


Fig.3

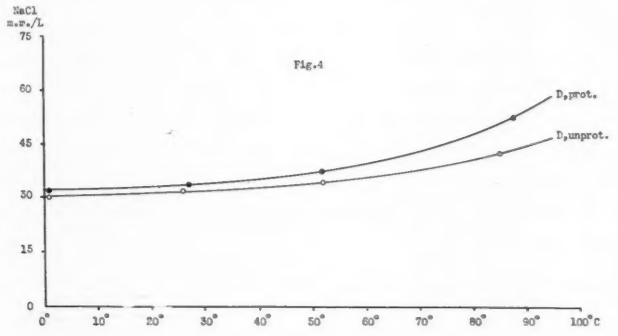


Fig.4

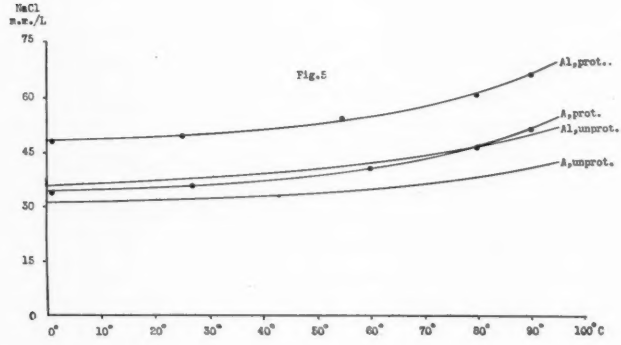


Fig.5

stability is most marked in the case of sol C, which sol was the least stable of all to electrolyte when undiluted.

The coagulation values were measured by placing separate 5 cc. portions of the sol and of the standard NaCl solution in stoppered test tubes and heating or cooling to the experimental temperature in a water bath. The contents of the tubes were mixed at the experimental temperature and allowed to stand for three minutes. The coagulation value was taken as that concentration of NaCl in the sol (expressed as millimoles per liter) which just produced a change from the normal red color of the sol to a deep violet blue. The color change is caused by an agglomeration of the gold particles and indicates incipient precipitation.

Effect of Temperature on Electrolyte-free Unprotected Gold Sols.

Unprotected sols containing no added electrolyte were found to coagulate spontaneously at temperatures between 150° and 250° C. The results are summarized in Table 1. The sols were held at the experimental temperature for 1 hour, unless as noted otherwise in the Table.

No regularity occurs between the dilution of the sols and their coagulation temperature. Coagulation of the sols was marked by the development of a fine, somewhat flaky, precipitate, usually deep blue in color, but occasionally violet-red. The solution itself became colorless.

The runs were made in 5 cc. portions in sealed 13 × 100 mm. Pyrex test tubes enclosed in steel pressure bombs of conventional design. The bombs were heated in an electric furnace. The degree of filling of the tubes and of the bombs was 0.7. Duplicate bomb runs were made at the critical coagulation temperatures.

Increase of temperature was found to have a peptizing effect on the hydrous aurous oxide sol E. The sol remained blue in color when it was heated at 100°, but became violet and finally pink when it was heated for 16 hours at 125°. The effect is probably caused by the reduction of the oxide to metallic gold. Gold hydroxide is partially decomposed in water to metallic gold at 135°.[3] The blue sol coagulated completely when held at 150° for 2 hours, and yielded a blue precipitate.

The temperature of spontaneous coagulation of copper sols has been found to decrease with decreasing charge on the parti-

[3] Morris, H. H.: Jour. Amer. Chem. Soc., vol. 40, p. 917, 1918.

TABLE 1.

SUMMARY: TEMPERATURE OF SPONTANEOUS COAGULATION OF GOLD SOLS.

S = Stable. C = Coagulated.

Time at experimental temperature = 1 hour, unless as indicated in parentheses.

Gold sol	Protected by silica sol	Silica in 5 cc. of sample	125°	150°	175°	200°	225°	250°	275°	300°	350°	410°
A						S	C	C		C		
A1						S	S	C				
A2						S	C	C				
A4				S	S	C	C	C				
B			S	S (2.5)	S	C						
B1			S	S (2.5)	C	C						
B2			S	S (2.5)	S	C						
C				S (2)		C		C				
C2						S		S				
C4				S (2)		C		C				
A	F	0.00286 g.				S				S	S (1.5)	
A1	F	0.00286 g.				S				S	S (1.5)	
A2	F	0.00286 g.				S				S	S (1.5)	C (2.5)
A4	F	0.00286 g.				S				S	S (1.5)	
A4	H	0.00129 g.									S (2.5)	
B	G	0.00045 g.								S	S (1.5)	
B	H	0.00129 g.									S (2.5)	
B1	G	0.00045 g.								S	S (1.5)	C (2.5)
B2	G	0.00045 g.								S	S (1.5)	

cles.[4] Increase of the charge, which can be effected in the case of gold by the addition of alkali to the sol, as described in a following section, and in other ways, would act to increase the resistance of a sol toward temperature.

Little information is available with regard to the general in-

[4] Deacon, B. R.: Jour. Phys. Chem., vol. 34, p. 1105, 1930.

fluence of temperature on colloidal systems. Freundlich [5] and von Buzagh [6] state that, as a rule, the stability of a sol increases with rising temperature, but the present experiments and those on colloidal copper cited above show that increase of temperature alone beyond some critical value results in coagulation. The factors brought into play by variation of temperature would include: the thermal movement of the particles; changes in the viscosity, polymerization and ionization of the dispersion medium; reaction or decomposition of the sol in the dispersion medium (*e.g.*, the hydrous aurous oxide sol described above); changes in the stability of the electrolyte adsorbed on the particles (noted in the case of the copper sol cited above); and changes in kind or adsorbability of the stabilizing electrolyte accompanying internal changes in a complex solution. As these factors vary, the stability of the sol, as reflected by its resistance toward electrolyte already in the sol or added from some outside source, will vary.

The mechanism of coagulation is determined by the probability of collision and the probability of adhesion of the dispersed particles. The former factor is influenced by the temperature and the concentration of the sol, and the latter factor by the charge on the particles. In general, increase of temperature alone, by increasing the number of particles having sufficiently high speed to penetrate on collision the charged repellent shell on the particles, favors coagulation. The charge on the particles would be largely influenced by the factors mentioned above. The greater the charge the less the probability of adherence and the more stable the sol.

Protecting Action of Colloidal Silica on Colloidal Gold.

According to Zsigmondy,[7] the gold number of silica is infinity, which means that a protecting effect is lacking. Elsewhere, Zsigmondy remarks [8] that aged silica sols with a strong opalescence (due to a large particle size) may have a protecting effect.

[5] Freundlich, H.: Colloid . . . Chemistry, p. 582, London, 1926.

[6] Von Buzagh, A.: Colloidal Systems, p. 281, London, 1937.

[7] Zsigmondy, R., and Thiessen, P. A.: Das Kolloide Gold, pp. 178, [illegible], Leipzig, 1925.

[8] Zsigmondy, R.: Kolloidchemie, p. 66, Leipzig, 1927.

If a gold compound is reduced in the presence of silica sol the formation of gold sol is notably favored.[9] Dialyzed silica sols also render more stable sols of Ag and other metals formed in them by reduction or electrical disintegration.[10] The effect is ascribed to the adsorption of the metallic salt by the silica particles, which hinders or prevents the growth of the reduced metal particles beyond the colloidal range of size. Colloidal gold is readily obtained by the reduction of gold salts in silica gel.[11]

Bastin[12] observed that 0.05 N auric chloride solutions were reduced to coarsely crystalline gold by chalcocite in the absence of gelatin or silica sol, but that sols were formed in the presence of these substances. These experiments were repeated by the writer, using 0.0005 N auric chloride solutions. Sol formation was found to be determined by the pH of the solution, and stable violet sols were obtained in the absence of gelatin or silica sol by making the solutions alkaline with K_2CO_3 or NaOH. Gelatin gives intense violet sols when boiled with auric chloride alone.

In the experiments described here, silica sol was found to protect colloidal gold both against electrolytes and against spontaneous coagulation on increase of temperature. The protection was found to be accompanied by a reversal of charge of the particles when in the presence of increasing concentrations of electrolyte.

An example to illustrate charge reversal by NaCl is given in Table 2. At low concentrations of added NaCl, the protected sols are negatively charged and stable; at intermediate concentrations the protected sols coagulate; at higher concentrations the sign of the charge is reversed to positive and the protected sols are again stable. The observations were made at 27° on gold sol A

[9] Küspert, F.: Ber. deutsch. chem. ges., vol. 35, p. 2815, 1902; Hiege, K.: Zeits. anorg. chem., vol. 91, p. 160, 1915.

[10] Freundlich, H.: Op. cit., p. 598.

[11] Ebelmen, J. J.: Compt. rend., vol. 25, p. 854, 1847; Davies, E. C. H., and Sivertz, V.: Jour. Phys. Chem., vol. 30, p. 1467, 1926; Holmes, H. N.: Jour. Phys. Chem., vol. 21, p. 708, 1917; Hatschek, E., and Simon, A. L.: Inst. Min. Met. Trans., 1912, p. 451.

[12] Bastin, E. S.: Jour. Wash. Acad. Sci., vol. 5, p. 64, 1915.

protected by silica sol F, in the ratio of 5 volumes of A to 1 of F. The nature of the sign on the particles was verified by observation of the cataphoretic movement between electrodes with a slit ultramicroscope.

TABLE 2.

CHARGE REVERSAL OF PROTECTED GOLD SOL.

NaCl conc. of sol, in mm./L.	0	30	35	40	50	120	180	240	480	3840	Sat'd
Color.....	Red	Red	Violet	Violet blue	Blue	Blue	Violet blue	Violet	Red	Red	Red
Zone.....	Negative, stable zone			Zone of coagulation				Positive, stable zone			

Protected sols in the second, positive, zone of stability cannot be immediately coagulated by any concentration of NaCl, and can be saturated with NaCl and boiled without coagulation. However, the reversed sols coagulate and deposit a loosely flocculent violet-red precipitate on standing from 3 to 20 days at 25°. The time decreases with increasing NaCl concentration.

The protected sols can also be reversed with HCl. The reversed sols cannot be coagulated in the second zone by any concentration of HCl, and remain stable after standing several months, at 25°, at acid concentrations as high as 8 N. With $CaCl_2$ and $AlCl_3$ the sols can be reversed and coagulated in the second zone by sufficiently high electrolyte concentrations.

Unprotected gold sols (negative) cannot be reversed by NaCl or HCl, but can be reversed by thorium nitrate and ferric, aluminum, lanthanum or thorium chlorides.[13] Negative silica sols are readily reversed by HCl. The theory of charge reversal, and the mechanism by which the charge on the gold particles is changed by electrolytes is discussed by Weiser.[14]

Experiments described on a later page show that the protecting action of silica on gold is increased by the addition of NaOH to

[13] Weiser, H. B.: Inorganic Colloid Chemistry, vol. 1, p. 88, New York, 1933.
[14] Weiser, H. B.: Op. cit., p. 88.

the sol, within a certain range of concentrations, and is decreased by the addition of HCl.

Effect of Temperature on the Coagulation Values of Protected Gold Sols.

The change with temperature of the amount of NaCl necessary to effect coagulation of protected sols A, B and D in the first, negative, zone of stability is represented in Figs. 2, 4 and 5.

Protected sol B was prepared by adding 1 volume of silica sol G to 5 volumes of gold sol B. Protected sols A and B were prepared by adding 2 volumes of silica sol F to 5 volumes of gold sols A and D. Sols A1 and B1 were prepared by adding silica sol to the diluted gold sols in the ratios cited. A slight correction was made in the measured coagulation values to allow for an increase in stability caused by the dilution of the original gold sol by the addition of the silica sol. The correction was calculated from the measured increase of stability effected by the first dilution of the corresponding unprotected sols.

At low temperatures the protected sols in the negative zone are hardly more resistant to NaCl than the unprotected sols, but the protecting action increases with temperature, and increases more rapidly than the increase of stability with temperature of the unprotected sols. The protecting action also increases with increasing dilution. Electrolytes other than NaCl were not investigated, but tests with KCl, $CaCl_2$ and $AlCl_3$ on sol B showed that a greater concentration was necessary to effect coagulation at 90° than at 27°. The general behavior is therefore the same.

The variation with temperature of the coagulation values of reversed, positive, sols for electrolytes other than NaCl was not investigated. It has already been noted that reversed sols do not immediately coagulate even when made 8 N or more in HCl, or when saturated with NaCl.

Effect of Temperature on Electrolyte-free Protected Gold Sols.

Gold sols protected by silica sol and containing no added electrolyte were found without exception to be stable at 350° C. The same sols when unprotected by silica coagulated at temperatures between 150° and 250°. Colloidal silica thus protects colloidal gold against spontaneous coagulation on increase of temperature. Those of the protected sols run at 410° were found to coagulate. The results are summarized in Table 1.

Experiments at temperatures up to 350° were made in 5 cc. portions in sealed 13 × 100 mm. Pyrex test tubes. Experiments at 410° were made in sealed silica glass tubes, enclosed in a chromium-tungsten alloy steel bomb. The silica sols used as the protecting agent, and the amount of silica actually present in the 5 cc. portions are cited in Table 1. The

Pyrex tubes were surficially devitrified at 300° and 350°, and an amount of material must have been leached from the glass and taken up by the sol. The Pyrex was found to be completely devitrified to a soft chalky material in 3.5 hours at 410°.

The degree of filling of the tubes and of the bombs was taken as 0.7 for temperatures up to 350°. Neither hydrophilic (lyocratic) colloids, in low concentrations at least, nor hydrophobic (electrocratic) colloids should have appreciable effect on the critical phenomena. Above the critical temperature the degree of filling of the tubes and the bombs may be taken as 0.33, the critical volume of water. The water in a concentrated hydrophilic sol may be largely associated with the micelles, and the critical phenomena may then be affected.

All but three of the seven runs made at 410° were lost by the bursting or leaking of the tubes while in the bomb, presumably due to slight inequalities in filling. The remaining sols, A (in duplicate) and B, developed a slight white turbidity and the gold was deposited as a pink film on the walls of the tube. Surprisingly, the film was not dissolved by prolonged treatment with hot aqua regia. Silica glass has been found to slowly gelatinize in water at 400°,[15] and the gold particles may be buried in a hardened gelatinous silica film opened on the surface of the glass.

Effect of NaOH and HCl on Protected and Unprotected Gold Sols.

As would be expected, the protected sols in the negative zone of stability are tolerant to NaOH and sensitive to HCl, while the opposite is true of the sols when in the positive zone of stability. The unprotected sols (negative) are tolerant to NaOH and sensitive to HCl.

A protected sol made by the addition of 1 volume of silica sol H to 5 volumes of gold sol B coagulated when made 0.77 N in NaOH at 25°. The same sol when unprotected was less tolerant and coagulated when made 0.38 N in NaOH. The protecting action of silica toward NaCl was increased by the addition of NaOH to the protected sols, within a certain range of NaOH concentrations. At alkalinities near the coagulation value for NaOH the protected sol was coagulated, in the negative zone, by the addition of an amount of NaCl less than the proper coagulation value. At lower concentrations of NaOH, however, the resistance of the sol toward NaCl was considerably increased. The addition of a few drops of 0.01 N NaOH to 5 cc. of the sol increased the coagulation value for NaCl from 34 to 40 mm./L.,

[15] Lenher, V., and Schrenk, W. T.: Jour. Amer. Chem. Soc., vol. 43, p. 393, 1921.

while in a sol made 0.32 N in NaOH the coagulation value increased almost two-fold, to 64 mm./L. A similar behavior was also found with the unprotected sols. When unprotected sol B was made 0.38 N in NaOH the coagulation value for NaCl increased from 32 to 48 mm./L. Further observations on the effect of alkali in favoring sol stability and sol formation are cited by Weiser.[16]

Protected sol B coagulated in the negative zone when made 0.010 N in HCl. The same sol when unprotected was slightly less tolerant and coagulated when made 0.009 N in HCl. The resistance of both protected and unprotected sols toward NaCl, in the negative zone, was found to decrease with increasing concentration of HCl. Negative, protected sols are readily reversed by HCl, but the unprotected sols cannot be so reversed. Protected sols reversed by HCl cannot be made negative again by the addition of NaOH; in such experiments an immediate red precipitate is obtained. Negative protected sols cannot be reversed by NaOH. Protected sols reversed by NaCl cannot be made negative again by the addition of NaOH; in such experiments a red precipitate is obtained, as above.

Both protected and unprotected sols containing added HCl rapidly become colorless when heated, even in acid concentrations as low as 0.05 N, due to solution of the gold. The ready solubility is owing to the extreme subdivision of the metal. In protected sols the acid strips the gold from the silica and leaves the latter dispersed as a positive sol. In the cold, protected sols reversed by HCl bleach considerably on standing a month or so, and more markedly in high acid concentrations, but still maintain a red tint.

Solubility of Silica.

In many of the experiments with the protected sols the silica was present in concentrations under the solubilities recently reported by Hitchen.[17] This raises the question whether the silica is in true solution or is dispersed in sol form.

[16] Weiser, H. B.: Op. cit., p. 51.

[17] Hitchen, C. S.: Inst. Min. Met. Bull., no. 364, p. 19, 1934.

To investigate this point, a silica sol was prepared by dilution of sol F which contained ½ the amount of silica reported soluble at 25°. This preparation was heterogeneous under the ultramicroscope, and coagulated, on standing, when saturated with NaCl. The sol as diluted had a silica content under that of any of the protected sols used in the experiments. Moreover, Moore and Maynard [18] have described experiments at room temperature with silica sols in concentrations of 30 parts per million which leave the colloidal nature of their preparations beyond doubt. The solubility at 25° reported by Hitchen is approximately 200 parts per million H_2O. It was also found that turbid silica sols could be diluted to a silica content ⅓ the reported solubility at 100° and be boiled without a decrease in turbidity.

The silica in the above preparations is, therefore, largely if not entirely colloidal, and the reported solubilities up to 100° cannot refer to silica in true solution. Since the protecting effect is maintained up to 350°, it appears probable that the silica is also colloidal at high temperatures. The protected sols contained from ¼ to 1/25 the amount of silica reported soluble at that temperature. While a substance in true solution may act to increase the stability of a sol—the effect of NaOH previously described is an instance—protection is usually conferred by a particle of colloidal size, which is inherently stable in the dispersion medium in question, *i.e.*, a lyo- or hydrophilic colloid, of which silica is one.

It is suggested that Hitchen and, earlier, Gruner,[19] have measured a peptization equilibrium that simulates a true solubility. It has been shown,[20] that a real temperature equilibrium exists between a coagulum of some hydrophilic colloids and the concentration of dispersed colloid in the liquid. The equilibrium is determined by the temperature, the particle size of the sol and the nature and concentration of electrolyte present. This means that the coagulum has a definite solubility, or more correctly a pepti-

[18] Moore, E. S., and Maynard, J. E.: Econ. Geol., vol. 24, pp. 391, 395, 513, 1929.

[19] Gruner, J. W.: Econ. Geol., vol. 25, p. 700, 1930.

[20] Weiser, H. B.: Op. cit., pp. 327–329.

zability, and affords a "solubility" curve similar to those where true solubility obtains.[21] Coagulums of different particle size give different "solubility" curves, the values increasing with decreasing particle size. This correlates with the increasing solubility found by Gruner for quartz, chalcedony and silica gel, in the order named.

In Hitchen's experiments a sample of precipitated amorphous silica was heated with a known volume of water in a steel pressure vessel and a portion of liquid withdrawn at the experimental temperature and analyzed for silica. The state in which the silica existed in the vessel, after it was extracted by the water from the coagulum was not shown, but it was remarked that the withdrawn portion was colloidal after it had cooled. This behavior was ascribed to the precipitation of silica from true solution; however, it is also in accord with the tendency of relatively pure silica sols to rapidly age and agglomerate into larger particle sizes (turbid suspensions), and would be expected if the sol followed down a peptization curve as it cooled.

DISCUSSION.

The derivation of hydrothermal solutions from an igneous melt and their subsequent history has been discussed by Fenner [22] and Bowen.[23] Following the main crystallization of the rock silicates, the residual liquid may boil off with the formation of an acid aqueous solution containing volatiles, heavy metals and silica as important constituents. The role of gaseous transfer here is stressed by Fenner. These solutions move outward from the intrusive, and by reaction with the wall rocks soon become neutral or alkaline. Later, the alkaline solutions may again become acid through internal changes generating H_2SO_4.[24] The special problem of the state in which the heavy metals are transported when the change to alkalinity occurs has been treated by Lindgren.[25]

[21] Weiser, H. B.: Op. cit., p. 329.
[22] Fenner, C. N.: Ore Deposits of the Western States, p. 58, New York, 1933.
[23] Bowen, N. L.: Idem, p. 106.
[24] Graton, L. C., and Bowditch, S. I.: ECON. GEOL., vol. 31, p. 674, 1936.
[25] Lindgren, W.: Op. cit., p. 9 et seq.

Transportation of the heavy metals as electrolyte presents no serious difficulties in acid solutions. Colloidal processes, of course, may also be operative. In the particular case of gold, the ready solubility in HCl found for the colloidal metal would preclude the formation of sols in hot solutions of any considerable acidity. The observations previously mentioned on the role of OH^- in determining sol formation and stability also point to the same conclusion. Gold is also soluble [26] in HCl containing auric chloride, ferric chloride (even in the presence of ferrous salts) or cupric chloride. Sheet gold is soluble in weak HCl at high temperatures and pressures.[27] Aqueous solutions of NaCl and KCl have been stated to be solvents of gold but this was not verified by Ogryzlo.[28] Auric chloride is stable in water up to about 450° when in the presence of alkali and alkaline earth chlorides.[29] It appears very probable that under acid conditions gold is carried in true solution.

If a dispersed colloid is present in the acid solutions, however, part or all of the dissolved gold salt may be adsorbed thereon. The adsorbability of gold salts by colloidal silica has already been remarked. The gold would then exist colloidally, although not as a colloid in its own right. The transportation and deposition of the gold would be determined by the special colloid chemistry of the adsorbing substance. Colloidal transportation of an electrolyte in this manner is illustrated by the several metacolloidal manganese oxide minerals, which may contain up to several per cent of K, Li, Ba, Cu, etc., as impurities adsorbed by the original sol.

With approaching neutrality or alkalinity of the originally acid solution, precipitation of the gold as native metal would be necessitated by reaction with hydrogen sulphide and other reducing agents and with sodium silicate.[30] The precipitated gold will

[26] Ogryzlo, S. P.: Econ. Geol., vol. 30, pp. 401, 415; Morris, H. H.: Op. cit., p. 921; Mellor, J. W.: Comp. Treatise Inorg. Chem., vol. 3, p. 528, London, 1923.

[27] Ogryzlo, S. P.: Op. cit., p. 413.

[28] Ogryzlo, S. P.: Op. cit., p. 415.

[29] Morris, H. H.: Op. cit., p. 924.

[30] In some brief experiments, it was found that auric chloride is decomposed to the metal by hot sodium silicate, with the formation of violet sols. Very concen-

now either be immediately thrown down and eliminated from the solution as a coarsely crystalline deposit, or be retained in the solution and transported as a dispersed colloid. That the gold is actually retained and carried in some form by neutral or alkaline solutions is shown by its abundant occurrence in the outer hydrothermal intensity-zones, and by its tendency for deposition toward the close of the paragenesis. The present experiments definitely indicate that gold sols protected by silica are stable in hydrothermal solutions at high temperatures and in the face of high concentrations of electrolytes. It may be remarked in this connection that in natural solutions the gold would be reduced in the presence of colloidal silica, which has been found to notably favor sol formation and stability.

The coagulation of gold sols carried in alkaline solutions may be effected in various ways. Decrease of temperature at constant electrolyte concentration would have a coagulating effect. Dilution at constant temperature of reversed sols would effect coagulation when the range of electrolyte concentrations corresponding to the intermediate zone of coagulation was reached. Further dilution to electrolyte concentrations in the first zone of stability would not repeptize the sol, as the gradual dilution would allow the particles to agglomerate into units too large to be redispersed while passing through the intervening zone of coagulalation. Dilution alone would not coagulate sols carried in the negative zone, but on the contrary would increase their stability.

Variation in the kind and concentration of electrolytes present, caused by mixing with other solutions or by internal changes in the solution itself, may effect coagulation in either zone. Since

trated, almost opaque, sols can be made in this way. The reaction (auto-reduction) involves the formation of sodium chloride, oxygen and metallic gold. The gold is protected by the colloidal silica present. The reported solubility of gold in Na or K silicate is believed by Boydell (Trans. Inst. Min. Met., 1924–25, p. 44) to be instead a peptization of the metal with stabilization with colloidal silica.

Sodium chloraurate undergoes partial reduction in cold sodium silicate (von Weimarn, P. P.: Koll. Zeits., vol. 11, p. 287, 1912). Gold is insoluble in Na_2S and Na_2S plus silica at 200° to 300° (Gruner, J. W.: Econ. Geol., vol. 28, p. 776, 1933), but is soluble in NaHS even at room temperature (Ogryzlo, S. P.: Econ. Geol., vol. 30, p. 420, 1935). It was not shown whether the NaHS solutions were colloidal or crystalloidal.

the sols are protected, the specific colloidal behavior of silica may be the principal factor influencing the deposition of the gold. A change from alkaline to acid conditions would also tend to coagulate the gold. With any considerable increase in acidity the gold would dissolve, unless agglomeration had progressed to a large, relatively insoluble, particle size. A slight increase in alkalinity of the solution would act to increase the stability of the protected sol.

Gold may also be removed from dispersion by the direct adsorption of the particles upon crystal surfaces exposed in the solution. If the adsorbing crystals are growing, the gold particles will be buried as finely divided inclusions. The adsorption may be selective between minerals of different species.[31] Gel surfaces may similarly remove colloidal gold from dispersion.

Further experimental work at high temperatures, using a pressure vessel fitted for the introduction and removal of material and permitting visual observation of the contents, would contribute greatly to a knowledge of the colloidal mechanisms by which gold may be transported and deposited in natural solutions. It would be desirable: (1) to investigate the characteristics of sols formed at high temperatures by reduction with H_2S, Na_2S and other inorganic reducing agents in the presence of colloidal silica, (2) to extend the measurement of coagulation values, for a variety of electrolytes and for protected sols in both the first and second zones of stability, up to 300°–400°, and (3) to find the effect of varying pH at constant temperature, and vice versa, on sol stability. The measurements in (2), above, should be made with decreasing temperature on sols formed at high temperatures, in order to simulate natural conditions. Sols formed at high temperatures may be acclimated, and behave differently on cooling than sols formed at low temperatures and heated.

SUMMARY.

(1) The stability of unprotected gold sols toward electrolyte (NaCl) increases with increasing temperature (Figs. 1–4).

[31] Frondel, C.: Amer. Min., vol. 22, p. 1104, 1937.

(2) The stability of unprotected gold sols toward electrolyte increases with increasing dilution of the sol (Figs. 1–3). The increase is not linear, but drops off at high dilutions. The temperature rate of change of stability remains about the same with dilution.

(3) Unprotected sols containing no added electrolyte coagulate spontaneously between 150° and 250° with increasing temperature (Table 1).

(4) Colloidal silica protects colloidal gold both against electrolyte and against spontaneous coagulation by increase of temperature. The protection is accompanied by a reversal of charge of the sol in the presence of increasing concentrations of electrolyte (Table 2).

(5) The protecting action of silica against electrolyte for sols in the negative zone of stability increases with increasing temperature, and increases more rapidly than the increase of stability with temperature of the unprotected sols (Figs. 2, 4, 5).

(6) The protecting action of silica against electrolyte increases with increasing dilution of the gold sol (Figs. 2, 5).

(7) Protected sols containing no added electrolyte are stable at 350° C., but coagulate spontaneously at 410° (Table 1).

(8) Protected sols in the negative zone of stability are tolerant to NaOH and sensitive to HCl, and the opposite is true of sols in the positive zone of stability. Unprotected sols behave similarly to negative protected sols, but the tolerance to NaOH is less, and the sensitivity to HCl is greater. The stability of negative protected sols toward electrolyte is increased by adding NaOH to the protected sol, within a certain range of NaOH concentrations, but is decreased by HCl.

(9) Silica sols are colloidal at 25° and 100°, and very probably up to 350°, in dilutions considerably under the solubilities recently reported by Hitchen and by Gruner. It is suggested that these investigators have measured a peptization equilibrium that simulates a true solubility, of the sort found for other hydrophilic colloids.

(10) The origin and subsequent history of hydrothermal

solutions is discussed with reference to the state in which gold is carried. In acid solutions the gold is very probably transported in true solution. Part or all of the gold salt, however, may be carried as adsorbed electrolyte on colloidal silica present in the solution. With approaching neutrality or alkalinity of the originally acid solution, the gold is precipitated out as a sol, protected by colloidal silica. The factors which may effect coagulation of the sols are briefly discussed.

ACKNOWLEDGMENTS.

The writer wishes to express his appreciation to Dr. Waldemar Lindgren for discussions of relevant geological matters; to Prof. E. A. Hauser for a critical reading of the manuscript and for discussions of experimental problems; and to Mr. Cortland Pearsall for assistance in instrumental work.

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Nov. 16, 1937.

OXIDIZED COPPER ORES OF THE UNITED VERDE EXTENSION MINE.*

G. M. SCHWARTZ.

ABSTRACT.

The ores of this deposit show an unusual amount of oxidation and secondary enrichment believed to have taken place during pre-Cambrian time. The ore minerals approximately in order of abundance are: chalcocite, cuprite, malachite, azurite, native copper, chrysocolla, pyrite, chalcopyrite, black oxide, covellite, and bornite. Primary sulphides are pyrite, chalcopyrite, and presumably bornite. The secondary sulphide ore is almost entirely chalcocite, but a little bornite and covellite are found. Malachite commonly replaced chalcocite directly but also replaced cuprite and occurs as nodular and boulder-like masses as well as in streaks in kaolinite. Azurite formed with malachite apparently in much the same sequence except that it was not found replacing sulphides. Cuprite directly replaces sulphides and is commonly replaced by malachite. Chrysocolla occurs mainly with malachite, and native copper also formed at places during oxidation.

No peculiarities or changes were noted that might be attributed to the pre-Cambrian age of the oxidation. The minerals, their sequence and textural relations seem entirely normal.

INTRODUCTION.

RECENTLY, through the courtesy of Mr. Olaf Hondrum, Chief Engineer, the Department of Geology of the University of Minnesota was supplied with an extensive suite of ores from the United Verde Extension mine. These ores are much oxidized and show many features touched on briefly in the writer's recent paper on the paragenesis of the oxidized ores of copper.[1] It seemed worth while to describe these ores in detail as an example of the paragenesis of oxidized copper ores of a single deposit.

The United Verde Extension ores are particularly interesting because secondary enrichment and most of the oxidation took place in pre-Cambrian time. Reber [2] says regarding this deposit,

* Presented before Society of Economic Geologists, Washington Meeting, Dec. 29, 1937.

1 ECON. GEOL., vol. 29, pp. 55–75, 1934.

2 Reber, L. E.: Geology and ore deposits of Jerome district. Am. Inst. Min. Eng. Trans., vol. 66, p. 4, 1922.

"The United Verde Extension possesses one of the largest known bodies of high-grade chalcocite ore, which is particularly noteworthy as the result of the only recorded instance of important secondary enrichment known to have taken place in pre-Cambrian time."

The writer is indebted to Mr. Olaf Hondrum for the valuable collection and for information regarding their occurrence; also to the United Verde Extension Mining Company for permission to publish results of the study.

Aid in preparation of polished and thin sections was rendered through funds granted by the Graduate School of the University of Minnesota. Special thanks are due to Dean Guy Stanton Ford who has generously supported the writer's research for many years.

SUMMARY OF THE GEOLOGY OF THE MINE.

Several papers have appeared on the Jerome district, but none is very detailed. Those by Reber,[3] Lindgren,[4] Ransome,[5] and Tenney[6] are most recent and include points covered in earlier discussions.

The United Verde Extension ore body lies on the hanging wall side of the great Verde fault. It is covered by about 850 feet of Paleozoic beds and Tertiary basalt, and is cut off at a depth of 2,000 feet by the Verde fault. The main ore body has an irregular pear-shaped form and is almost surrounded by schistose quartz porphyry in which it formed mainly by replacement. Other rocks found in the mine are greenstone schist and diorite. Reber believes the ore to have been localized by a fissure or shear zone nearly at right angles to the schistosity.[7]

Tenney states that the pre-Devonian outcrop consists of a thoroughly leached siliceous gossan containing almost no copper.

[3] Reber, L. E.: *Op. cit.*

[4] Lindgren, W.: Ore deposits of the Jerome and Bradshaw Mountain Quadrangles, Arizona. U. S. Geol. Surv. Bull. 782, 1926.

[5] Ransome, F. L.: Ore deposits of the Southwest. XVI Int. Geol. Cong. Guidebook 14, pp. 20–22, 1932.

[6] Tenney, J. B.: Copper resources of the world. XVI Int. Geol. Cong., vol. 1, pp. 179–189, 1935.

[7] Reber, L. E.: *Op. cit.*, p. 23.

This was true only of the main ore body. To the north several big masses of chalcocite were found. The trough of the post-sediment erosion channel was deepest directly above the main ore body, which may account for this part of the gossan being barren. The deposit is believed to have remained buried since Cambrian time.

It is generally accepted that the United Verde Extension ore body is a faulted and eroded remnant of the United Verde ore pipe, and Ransome [8] shows five diagrams representing conditions from pre-Cambrian to the present time.

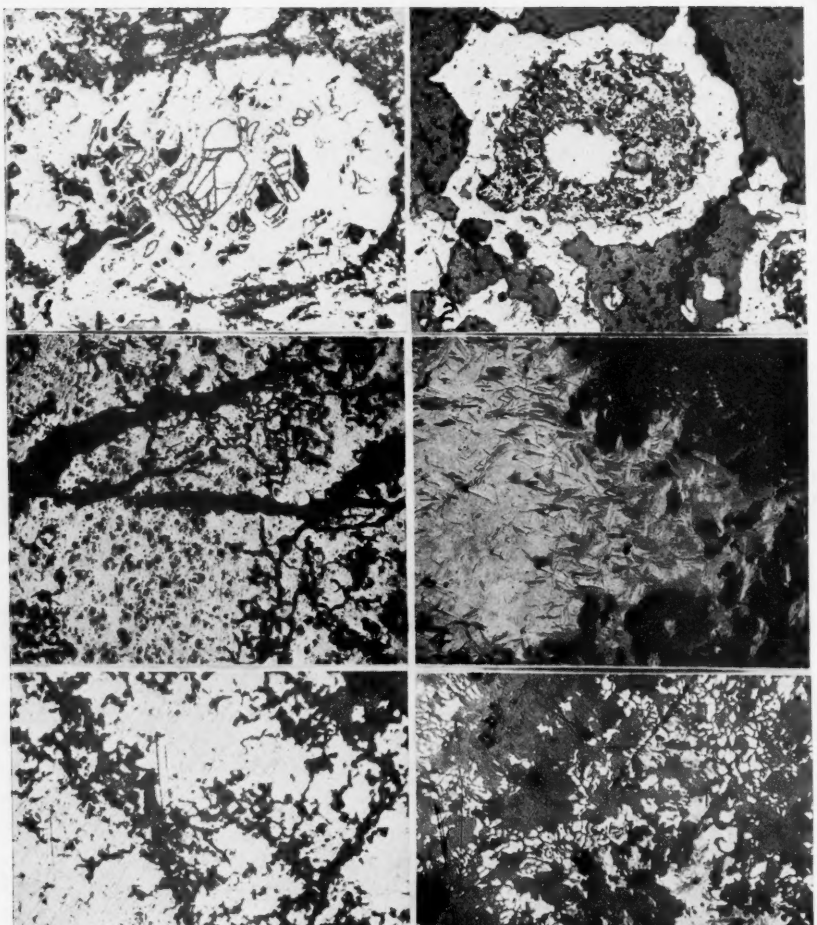
Most of the reports describe the main ore body. Near the top, on the 1,300 level, cuprite and native copper were abundant, especially near the southern edge where the wall rock was kaolinized porphyry. From the 1,400 level down, the oxide was absent and the typical ore was a mixture of chalcocite and pyrite with some chalcopyrite. This deposit bottomed fifty feet below the 1,600 level.[9] Below the 1,500 level only the core of the ore body was enriched and mined for copper values. The fringes were primary loose pyrite carrying about one percent copper and were mined for flux. From the 1,600 level down, little or no enrichment had taken place, but as the copper values decreased, so also did the insoluble content, so that the material made good iron flux.

Several hundred feet north of the main ore body was a large mass of pyrite entirely different from the loose pyrite associated with the main ore body. It carried less than one percent copper but contained nearly ten per cent. CaO and not more than five per cent. insoluble, so it was mined for flux to smelt the high grade oxidized ores that carried forty to fifty percent insoluble. This pyritic ore was hard and firm and extended from the 1,500 to 1,900 levels where it dwindled to narrow stringers. On the 1,600 level it had dimensions roughly 150 feet by 150 feet and carried two to four percent zinc in contrast to the main ore body that contained no zinc.

The ores described in this paper largely came from numerous

[8] Ransome, F. L.: XVI Geol. Cong. Guidebook 14, Plate 4, 1932.

[9] Hondrum, O.: Personal communication.



FIGS. 1–6.

smaller ore bodies and lenses. Mr. Hondrum[10] reports that south of the main ore body and 200 to 300 feet higher were several fracture zones in schist and schistose porphyry that contained high grade ore. The chalcocite in these lenses has been extensively oxidized and both malachite and azurite are abundant. In a large mass of quartz to the northwest of the main ore body several masses of residual chalcocite were found with considerable hematite and some cuprite.

The ore minerals identified in the ores studied, approximately in order of abundance, are: chalcocite, cuprite, malachite, azurite, native copper, chysocolla, pyrite, chalcopyrite, black oxide, covellite, and bornite. Associated minerals include quartz, kaolinite, "limonite" and hematite.

The ore varies from massive, nearly pure chalcocite to chalcocite extensively veined by malachite and a variety of nodular concretionary and boulder-like masses of malachite, azurite, and "limonite." Vugs lined with mammillary masses of malachite and good crystals of azurite are common. The variety is so great that proper characterization is difficult except by detailed descriptions.

Primary Sulphides.—The only primary sulphides recognized in the suite of ores examined are pyrite and chalcopyrite, and possibly bornite. Previous writers have evidently also failed to note other minerals as none seem to be mentioned in the literature and the absence of sphalerite, a common mineral in the United

FIG. 1. Rounded aggregate of chalcocite with remnants of pyrite. × 120.

FIG. 2. Spheroidal aggregate of chalcocite with zone of limonite. Quartz, dark gray. Probably a replacement of pyrite by chalcocite and limonite. × 120.

FIG. 3. Dendritic veinlets of cuprite (dark gray) in chalcocite (white). × 120.

FIG. 4. Covellite, light gray blade-like crystals in chalcocite (light) near contact with malachite (dark). × 60.

FIG. 5. Dendritic veinlets of malachite (gray) in chalcocite (white). × 100.

FIG. 6. Chalcocite (white) remnants in malachite (gray). × 100.

[10] Personal communication.

Verde mine, has been emphasized. Pyrite occurs in the ore only as small remnants in chalcocite (Fig. 1). Pyrite evidently was abundant locally as Ricard [11] notes that the ground above the 1,300 foot level contained rich copper ore with an overburden of crumbly pyrite.

There is abundant evidence in the chalcocite that it replaces pyrite leaving crude pseudomorphs and pisolitic areas in which pyrite may or may not remain.

Lindgren [12] shows two photomicrographs of ore from the 1,650-foot level with more abundant pyrite than any the writer happened to have, and describes the occurrence of massive pyrite as well as much pyrite concealed by chalcocite. This type of ore as noted above was typical of the main ore body. Chalcopyrite is scant in the polished ores and this seems to agree with all previous descriptions of the mine. There is no reasonable doubt, however, that chalcopyrite was an important mineral of the primary ore. Analogy with the United Verde ore would indicate this, and the fact that chalcopyrite occurs as remnants in chalcocite ore without evidence of any earlier mineral, even pyrite in some cases, seems adequate proof of the original importance of chalcopyrite. Chalcopyrite is clearly cut by veinlets of chalcocite that replaced it directly without going through the intermediate bornite stage as it commonly does. The scarcity of bornite in the ores studied is a striking feature, but the mineral has been recorded in the ore body by Reber.[13] It was noted by the writer in only two specimens and in these it appears to be secondary as it occurs with chalcopyrite largely replaced by chalcocite.

Chalcocite.—The importance of chalcocite in the United Verde Extension has been emphasized in every description of the ore. The common type is massive, fine grained, orthorhombic chalcocite. On polished surfaces this generally shows the well developed and characteristic pisolitic structure referred to above (Fig. 2). This structure is believed to have developed during

[11] Ricard, T. W.: The study of the United Verde Extension, Min. and Sci. Press, Vol. 116, p. 52.

[12] *Op. cit.*, plate 13 and p. 84.

[13] *Op. cit.*, p. 18.

the gradual replacement of pyrite by the chalcocite. In some specimens chalcocite seems to have imperfectly replaced pyrite which was later altered to "limonite" (Fig. 2).

Much of the massive chalcocite in the suite examined in this study is extensively replaced by cuprite and malachite (Figs. 3–6). In the early stages the chalcocite is cut by a few veinlets but in the more advanced stages an extreme dendritic form is developed and then the chalcocite seems to have broken down rapidly over large areas and innumerable small remnants remain especially in malachite (Fig. 6). It was repeatedly noted that lath-shaped or needle-like crystals of chalcocite commonly appeared around solid areas of malachite. This gives the impression of having developed in the malachite, possibly by some rearrangement during carbonation.

Covellite.—Lindgren [14] noted that covellite was of localized occurrence but that large specimens of covellite were obtained. In the oxidized ores covellite occurs sparingly, but feathery or lath-shaped crystals are not uncommon in chalcocite near the contact with replacing malachite (Fig. 4). The chalcocite in and near the covellite is conspicuously mottled, suggesting solid solution of some of the cupric sulphide to give the mottled effect noted by many previous writers.

Malachite.—Malachite is not mentioned as important in any of the previous descriptions cited above, but in the suite of 26 large specimens examined, it is a conspicuous and important mineral. It commonly forms, as noted above, directly from chalcocite varying from incipient to almost complete replacement of chalcocite. It also occurs in nodular and boulder-like masses, which in part may well represent copper that was transported rather than chalcocite or cuprite carbonated in place. Cuprite generally shows some alteration to malachite; mostly it is extensively replaced.

Malachite occurs as streaks and veinlets in kaolinite, commonly penetrating this mineral in a most complex manner. It also occurs as radiating aggregates in more or less massive azurite. It

[14] *Op. cit.*, p. 85.

commonly replaces chalcocite, which breaks down readily to form malachite and thus a very dendritic pattern is developed rather than simple veinlets as is common in replacement of one sulphide by another. Veinlets of late malachite generally cut across most other minerals.

Azurite.—In many oxidized copper ores azurite is a common associate mineral with malachite (Fig. 7) as has been recently

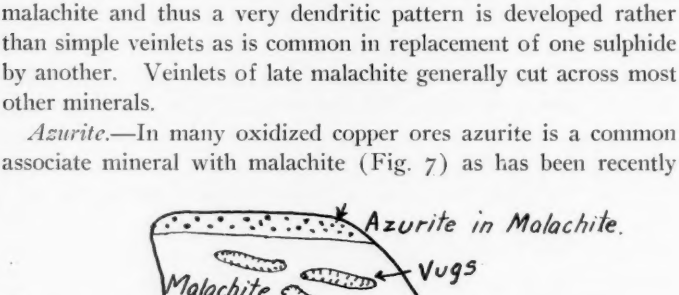


FIG. 7. Sketch of polished surface of oxidized ore showing complex relation of malachite, azurite and chrysocolla. × 1.

described by the writer.[15] The characteristic occurrence of this mineral in ores in general is duplicated almost exactly in the United Verde Extension ores. In nodular ores more or less alternating deposition with malachite is common, with some late azurite as is evidenced by the common occurrence of good crystals lining vugs. It is also usual to find small radiating spherical aggregates of azurite irregularly distributed in certain areas of malachite and similar aggregates were noted in limonitic clay.

The radiating nodular masses of azurite show variation in intensity of the blue color in concentric bands.

Azurite with malachite compose peculiar nodular or boulder-like masses of ore, one of which is illustrated in Fig. 9. The outside of the mass is a thin zone of malachite about one-tenth inch wide. The zone of azurite varies from one-fourth to nearly

[15] ECON. GEOL., vol. 29, p. 62, 1934.

one-half inch in width with a band of azurite cutting across the specimens obviously along a crack. The inside is soft earthy "limonite" with some small aggregates of azurite throughout. Another somewhat larger mass shows even more complicated relations with an outside of mixed porous "limonite" and malachite and a zone of nearly pure azurite with a central part about two inches across composed of limonite-stained cherty material with spherical aggregates of azurite.

Cuprite.—In most of the oxidized ores cuprite is fairly abundant in a disseminated earthy type. As noted above it commonly occurs as dendritic veinlets replacing chalcocite. Chalcopyrite was observed surrounded by chalcocite, this in turn surrounded by earthy cuprite, which largely eroded out during polishing even when the no-relief method was used. Some specimens have been altered almost entirely to cuprite, presumably where protected from carbonate waters.

Pisolitic chalcocite commonly shows associated cuprite, generally as a rim surrounding a core of chalcocite, and in turn is surrounded by chalcocite. This type shows many varied relations of cuprite and chalcocite causing one to speculate as to the conditions that led to such complicated relations of oxide and sulphide.

Native Copper.—During oxidation of copper ore bodies, a little native copper is generally formed; rarely, it is extensive. The latter seems to have been the case in the United Verde Extension ores especially near the top of the lenses where oxidation was most extensive, that is, on and below the 1,300 level of the main ore body. In general, the ores examined during this study were too highly carbonated to show much native copper, but one large specimen (Fig. 8) a flat slab about one inch thick, showed abundant native copper as irregular remnants in cuprite. The cuprite varies from massive crystalline material to well formed crystals lining vugs; it is clearly later than the native copper but it does not necessarily follow that all of the cuprite formed from native copper.

Chrysocolla.—The general descriptions of the mine fail to describe the occurrence of chrysocolla. From the writer's experi-

ence it may be concluded that this was due to the abundance of malachite, which in general masks the chrysocolla so that it becomes apparent only after careful examination. Microscopic

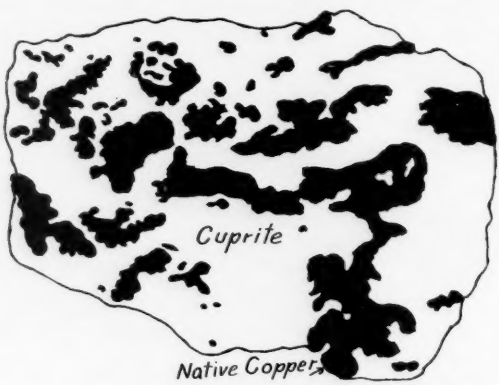


FIG. 8. Sketch of polished surface showing relation of cuprite and native copper. × ½.

examination, however, proves chrysocolla to be generally associated with malachite (Fig. 7) and its occurrence is typical of the confused aggregates of varieties previously described by the writer.[16]

Other Minerals.—Quartz and kaolinite in considerable abundance were found in the ores studied and these are described by previous writers.

Ricard [17] noted that the main ore body was bounded on the east and north by a kaolinized selvage and later writers have mentioned that kaolinization of the rocks is so pronounced that in places it has masked their original character. One large specimen at hand seems to be entirely pure white kaolinite except for veinlets of malachite and azurite. X-ray determination of the white material shows only the kaolinite pattern. Other kaolinitic masses show mainly azurite as a later mineral and still others show some

[16] ECON. GEOL., vol. 29, p. 65, 1934.

[17] *Op. cit.*, p. 49.

residual sulphides, chalcopyrite, chalcocite, with cuprite and iron oxide.

Commonly kaolinite is impregnated by azurite and malachite imparting a blue or green color to material that is low in copper content.

Quartz in various forms is locally abundant in the ore. Lindgren [18] noted fine grained cherty quartz as a phase of the mineralized material, and Reber [19] noted jaspery quartz and also mentions more or less quartz in the chalcocite zone. Hondrum [20] states that in the leaner portions of the main ore body, a decrease in silica also means a decrease in copper. In the pyrite bottom of the main ore body the insoluble content is only one or two percent whereas in the enriched portions, insoluble runs as high as forty percent with an average of around thirty to thirty-five percent.

Quartz shows up on polished surfaces even where none is suspected in hand specimen. In certain specimens quartz forms a matrix to chalcocite with a result that appears much like the texture of sandstone. In other specimens chalcocite forms a matrix to quartz grains. Quartz is commonly cut by fractures filled with malachite presumably deposited by oxidizing solutions rather than alteration of copper minerals in place. The concentric forms of chalcocite referred to above are generally associated with much quartz. Presumably this material was originally quartz and pyrite. Very fine cryptocrystalline or chalcedonic quartz was also noted in close association with chrysocolla.

"Limonite" is present, at least in small amounts, in most specimens. In general it seems to have formed at a late stage as it is (as a rule) found as an earthy filling in vugs (Fig. 9) where it may form the main mineral, or coat malachite or azurite. It is commonly mixed with kaolinite to form a brownish limonitic clay.

Paragenesis.—The formation of the minerals of the ores seems to follow a fairly normal and definite pattern.

[18] *Op. cit.*, p. 85.
[19] *Op. cit.*, p. 15.
[20] Personal communication.

The primary minerals now recognizable are pyrite, chalcopyrite, and quartz. Supergene enrichment largely converted both pyrite and chalcopyrite to chalcocite with a little bornite. Oxidation

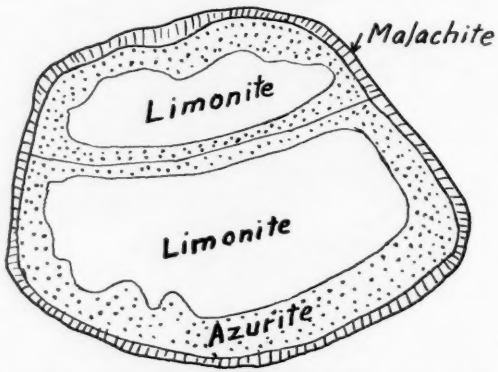


FIG. 9. Sketch of interior of nodule of oxidized ore sawed through center. × ¾.

in turn converted the chalcocite to cuprite or directly to malachite. Cuprite is commonly replaced by malachite. Azurite is a common associate of malachite but does not seem to have replaced either sulphide or cuprite directly, but formed with and sometimes after malachite, probably from copper bearing carbonate waters because good crystals of azurite commonly line vugs.

"Limonite" formed as a result of the oxidation of pyrite and chalcopyrite. Some of it evidently rather late in the alteration. Native copper formed in connection with extensive cuprite probably where oxidation was intense and carbonate solutions unimportant.

The formation of nodular and pisolitic structures is a characteristic feature of enrichment and oxidation.

The writer rather expected a complicated paragenesis because of the pre-Cambrian age of the oxidation. It might be logically expected that changes in the rather easily altered minerals of the oxide zone would have taken place during the long interval be-

tween pre-Cambrian time and the erosion which brought the ore near the present surface. No unusual changes were found and insofar as the writer can determine, very little, if any, change took place since pre-Cambrian oxidation.

UNIVERSITY OF MINNESOTA,
MINNEAPOLIS, MINN.,
October 15, 1937.

THERMODYNAMICAL CALCULATION OF THE SOLUBILITY OF SOME IMPORTANT SULPHIDES, UP TO 400° C.

JEAN VERHOOGEN.

ABSTRACT.

Usual methods of physical chemistry have been applied to the calculation of the solubility of sulphides up to 400° C. Results for ZnS, PbS, HgS, CuS, Ag_2S, and Cu_2S, indicate a considerable increase of the solubility with temperature, the ratio $\frac{\text{solubility at } 400°}{\text{solubility at } 25°}$ ranging from 10^2 to 10^4, and reaching even 10^7 for zinc sulphide. The order of increasing solubility remains practically the same at 400° as at 25°. A convenient formula has been developed, giving changes of solubility with acidity.

INTRODUCTION.

In regard to the geological significance attached to the knowledge of the solubility of sulphides at high temperature, it is perhaps surprising that no accurate data on this matter should be available as yet. Several attempts have been made to determine the variation of solubility with temperature,[1] none of which appear to be wholly satisfactory, from a theoretical point of view. As the measurement of the solubility at high temperature must be carried out under pressure in order to prevent the ebullition of the solvent, experimental difficulties are considerable, and the problem may perhaps be more easily attacked from the theoretical side.

Thermochemistry, being concerned with the thermal changes that accompany reactions, provides methods by which these changes may be calculated, provided numerical values of certain important thermodynamical functions are known. As these methods, although of common use in chemistry, may seem unfamiliar to geologists, a few theoretical considerations will be given first.

[1] Foreman, F.: Econ. Geol., vol. 24, pp. 811–37, 1929. Kordes, E.: Min. Petr. Mitt., vol. 46, pp. 256–88, 1935.

The equilibrium between a solid and its saturated solution obeys the well-known Van't Hoff law

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}, \qquad (1)$$

where K is the equilibrium constant at the temperature T, and ΔH is the heat absorbed when one mole of the substance goes into solution at the temperature T.[2] If c_1 and c_2 are the solubilities at the temperature T_1 and T_2, and if ΔH remains constant throughout the temperature interval $T_1 - T_2$, equation (1), integrated, becomes

$$\ln \frac{c_2}{c_1} = \frac{\Delta H(T_2 - T_1)}{RT_1T_2}.$$

Thus the solubility at any temperature T_2 may be calculated when ΔH, c_1 and T_1, are known. It may be noticed that if heat is absorbed when the substance goes into solution ($\Delta H > 0$), for $T_2 > T_1$, $\ln (c_2/c_1) > 0$, *i.e.*, the solubility increases with increasing temperature.

The values of ΔH for sulphides given in the tables cannot be relied upon, as they probably refer to solubility data which, according to Kolthoff,[3] are erroneous. Besides, the integrated form of equation (1) disregards the fact that ΔH changes with temperature, and may thus be applied only within narrow limits. For these two reasons, a better method of calculating changes of solubility with temperature should be sought. As the free energy is the only function for which data that enable us to calculate its changes with temperature are available, it will be necessary to develop first a convenient method by which solubilities may be calculated from free energies. A definition of free energy will be given in due course.

SOLUBILITY PRODUCT.

Suppose that a molecule of a substance going into solution is entirely dissociated in ν_- anions and ν_+ cations. If c is the concentration of a saturated solution of this substance *i.e.*, its solubility

[2] Throughout this paper R represents the gas constant 1.98 cal./1°.

[3] Jour. Phys. Chem., vol. 35, p. 2711, 1931.

in moles per liter, c_-, concentration of the anions will be equal to $\nu_- c$, and that of the cations, c_+, will be $\nu_+ c$.

The solubility product P is defined as the relation

$$P = (c_-)^{\nu-}(c_+)^{\nu+}$$

or

$$P = (\nu_-)^{\nu-}(\nu_+)^{\nu+} c^{\nu-+\nu+} . \qquad (2)$$

The concentrations of the ions of a salt are always such that

$$(c_-)^{\nu-} \cdot (c_+)^{\nu+} \leqslant P.$$

If the initial concentrations are such that $(c_-)^{\nu-} \cdot (c_+)^{\nu+} > P$, the salt will precipitate out of the solution until the concentrations have reached the right value defined by (2). On the contrary, a substance will keep on going into solution as long as the concentrations are such that $(c_-)^{\nu-} \cdot (c_+)^{\nu+} < P$.

In the case of silver chloride, for instance, $\nu_+ = 1$, $\nu_- = 1$; thus $P = c^2$. For zinc chloride $ZnCl_2$, $\nu_+ = 1$, $\nu_- = 2$, and $P = 4c^3$. These are instances of very simple relations between the solubility c and the solubility product P.

The following data on the solubility and solubility product of sulphides have been compiled from Ravitz.[4]

TABLE I

SOLUBILITY PRODUCT AND SOLUBILITY OF SULPHIDES AT 25° C.

	P.	c (moles per liter).
ZnS	$1.15\ 10^{-26}$	$1.47\ 10^{-9}$
PbS	$7.00\ 10^{-30}$	$3.62\ 10^{-11}$
CuS	$3.48\ 10^{-38}$	$2.55\ 10^{-15}$
Ag_2S	$3.28\ 10^{-52}$	$2.48\ 10^{-15}$
HgS	$1.00\ 10^{-47}$	
Cu_2S	$3.60\ 10^{-50}$	$1.19\ 10^{-14}$

There is an apparent discrepancy between data of the first and second columns of Table I: the solubility of zinc sulphide is not equal to the square root of the solubility product; nor is it for any other sulphide listed in the table. This arises from the fact that the ion $S^=$ is most readily hydrolized according to the equation

$$S^= + H_2O \rightleftharpoons HS^- + OH^-$$

and further

$$HS^- + H_2O \rightleftharpoons H_2S + OH^-.$$

[4] Jour. Phys. Chem., vol. 40, pp. 61–70, 1936.

These secondary reactions alter considerably the concentration of the anion $S^{=}$ and the simple relation $P = c^2$ holds no longer. It will be necessary to work out a relation that will take into account the presence of HS^- and H_2S in the solution.

Consider first the sulphides of bivalent metals (ZnS, PbS, etc.). It is obvious that the number of moles of the metal that have gone into solution will always be equal to the total number of moles of sulphur and since the sulphur may exist as $S^{=}$, HS^-, or H_2S,

$$(M^{++}) = (S^{=}) + (HS^-) + (H_2S), \tag{3}$$

brackets designating concentrations in moles per liter. By definition

$$(M^{++})(S^{=}) = P.$$

Put

$$K_1 = \frac{(H^+)(S^{=})}{(HS^-)}$$

and

$$K_2 = \frac{(H^+)(HS^-)}{(H_2S)},$$

K_1 and K_2 being the equilibrium constants of the reactions

$$HS^- \rightleftharpoons H^+ + S^{=} \tag{4}$$

and

$$H_2S \rightleftharpoons H^+ + HS^-. \tag{5}$$

Substituting values of P, K_1, and K_2, in (3):

$$(M^{++}) = (S^{=})\left(1 + \frac{(H^+)}{K_1} + \frac{(H^+)^2}{K_1K_2}\right)$$

or

$$(M^{++})^2 = PX \tag{6}$$

with

$$X = 1 + \frac{(H^+)}{K_1} + \frac{(H^+)^2}{K_1K_2}.$$

At 298° K., $K_1 = 10^{-15}$ and $K_2 = 1.15\ 10^{-7}$.[5] If the solution is neutral, $(H^+) = 10^{-7}$. Then $X = 1.87\ 10^8$ and

$$(M^{++}) = 1.37\ 10^4\sqrt{P}$$

[5] International Critical Tables, vol. 7, p. 237, 1931.

(M^{++}) is obviously equal to the solubility c. For zinc sulphide, $P = 1.15\ 10^{-26}$, thus $c = 1.37\ 10^{4}\sqrt{1.15\ 10^{-26}} = 1.47\ 10^{-9}$, which is the value given in table I.

Turning now to sulphides of monovalent elements, there is an equation similar to (3)

$$2(M^{+}) = (S^{=}) + (HS^{-}) + (H_2S).$$

As

$$P = (M^{+})^2(S^{=})$$

it can easily be shown that

$$2(M^{+}) = (S^{=})X$$

or

$$2(M^{+})^3 = PX.$$

Finally

$$(M^{+}) = \sqrt[3]{\frac{PX}{2}}. \qquad (7)$$

In a neutral solution at 298° K., $X = 1.87\ 10^{8}$. For silver sulphide, $P = 3.28\ 10^{-52}$; thus the solubility of silver sulphide, expressed in moles of silver per liter of solution, will, be

$$c = \sqrt{\frac{3.28\ 10^{-52} \times 1.87\ 10^{8}}{2}} = 3.1\ 10^{-15}.$$

Equations (6) and (7) may be easily applied to determine changes of solubility as function of the acidity of the solution. Numerical values of the solubility of zinc and silver sulphides in acid, neutral, and alkaline, solutions will be found in Table II:

TABLE II.

SOLUBILITIES AT 25° C., MOLES OF SULPHIDE PER LITER.

	ZnS.	Ag_2S.
pH = 3	$1.00\ 10^{-5}$	$5.6\ 10^{-13}$
pH = 5	$1.00\ 10^{-7}$	$2.6\ 10^{-14}$
pH = 7	$1.47\ 10^{-9}$	$1.5\ 10^{-15}$
pH = 9	$1.07\ 10^{-10}$	$2.7\ 10^{-16}$
pH = 11	$1.07\ 10^{-11}$	$5.9\ 10^{-17}$

In fig. 1, solubilities have been plotted against acidity. From the slope of these curves it appears that equal changes in acidity

produce greater changes in the solubility of zinc sulphide than in that of silver sulphide. Changes in the acidity of a saturated solution may be sufficient to cause a selective precipitation of the sulphides.

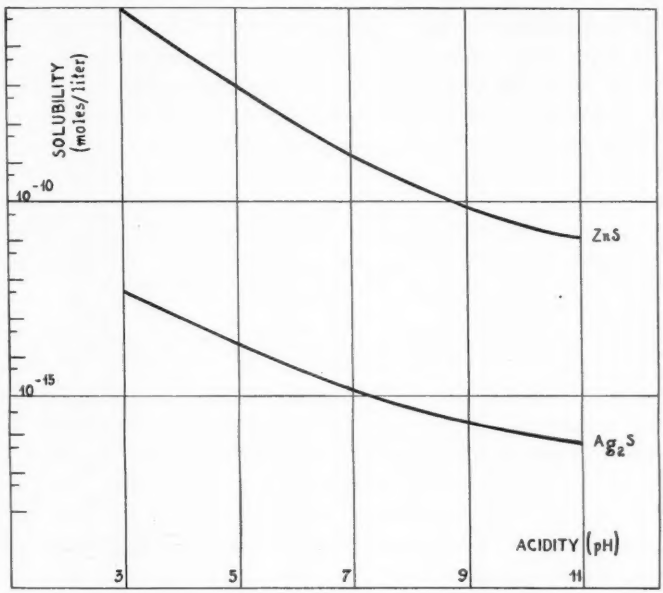


FIG. 1.

FREE ENERGY.

Before proceeding to establish a relation between solubility product and free energy, it may be necessary to recall briefly a few facts concerning free energy and its definition.

It is common experience that a given reaction may proceed in widely different ways. For instance, if a slab of zinc is placed in a solution of hydrochloric acid, hydrogen will be evolved, zinc will go into solution, and a considerable amount of heat will be given off. This reaction is an irreversible one, for it is obvious that heating a solution of zinc chloride will not be sufficient to precipitate

the zinc out of the solution. On the contrary, if the slab of zinc happens to be connected electrically through an external circuit to another electrode in the same solution, the same reaction, *i.e.*, the formation of zinc chloride and the evolution of hydrogen, will take place in a reversible manner; current will flow through the circuit and work may be performed by an electric motor. The reaction is reversible because if work is applied to the motor, the current will reverse its direction, hydrogen will go into solution at the hydrogen electrode and zinc will precipitate at the zinc electrode.

The heat content H of a system is defined as

$$H = E + pv, \tag{8}$$

E being the internal energy, p the pressure, and v the volume. By definition, the free energy F of a system is

$$F = H - TS, \tag{9}$$

S being the entropy [6] and T the temperature. The maximum work A is

$$A = E - TS. \tag{10}$$

From (8), (9), and (10), it follows that

$$F = A + pv. \tag{11}$$

Let us consider a system passing from an initial to a final state through a reversible isothermal reaction. Denoting by ΔA, ΔE, ΔS, the changes of the function A, E, and S, during this transformation, we may write, according to (10):

$$\Delta A = \Delta E - T\Delta S.$$

Now, $T\Delta S$ is, by definition, the heat exchanged with the surroundings during this reaction. It follows from the first theorem of thermodynamics that $-\Delta A$ must represent the amount of work performed by the system.

Returning to the zinc slab connected to the hydrogen electrode, the work $-\Delta A$ performed during the process is of two kinds: there

[6] The variation of the entropy of a system during a reversible isothermal process is defined as the ratio of the heat exchanged with the surroundings to the temperature at which the reaction is taking place.

is the work performed by the electric motor, and their is the work done against the external pressure by the evolving hydrogen. At constant pressure, this work against the external pressure is pdv, dv being the change in volume. The work performed by the motor must thus be equal to $-\Delta A - pdv$ or, according to (11), to $-\Delta F$. $-\Delta F$ may be described as the amount of work available for practical uses and is called accordingly the "free" energy.[7]

For every mole of zinc going into solution, 2 faradays or $2 \times 96{,}500$ coulombs travel through the external circuit. If E is the difference of potential between the two electrodes, the work developed by the motor will be $2 \times 96{,}500 \times E$ coulombs per volts or $2 \times 23{,}060 \cdot E$ calories per volt. The free energy of ionization at the temperature T of an element of valence n will be

$$-\Delta F = nE \times 23{,}060 \text{ cal./volt}, \qquad (12)$$

E being the normal potential of this element at the temperature T.

Let us return once more to the reversible reaction discussed above. It is obvious that as long as a condition of equilibrium has not been reached, zinc will keep on going into the solution, current will keep on flowing through the external circuit, and work will be available. This work, or the free energy $-\Delta F$, will drop to 0 only when the current ceases to flow, *i.e.*, when a state of equilibrium has been reached, the solution being saturated with zinc.

It may be shown that for any reaction proceeding at finite speed, thus irreversibly, $-\Delta F$ is either > 0 or < 0. The relation $\Delta F = 0$ is sufficient to ascertain that the reaction proceeds with infinite slowness; *i.e.*, that a condition of equilibrium has been reached. The direction in which a reaction takes place depends on ΔF: if $-\Delta F > 0$, work is available and the reaction may occur spontaneously; if $-\Delta F < 0$, the reaction reverses its direction.

Free energies, like heats of reaction, are additive. If ΔF_1 is the free energy change of the reaction

$$A \rightleftharpoons B$$

[7] Lewis, G. N., and Randall, M.: Thermodynamics and free energy of chemical substances, p. 155, New York, 1923.

and if ΔF_2 is the free energy change of the reaction

$$B \rightleftarrows C$$

the free energy change of the reaction

$$A \rightleftarrows C$$

will be $\Delta F_1 + \Delta F_2$.

The free energy of an element in its standard state at ordinary pressure and at a chosen temperature is arbitrarily taken as 0. It follows that the free energy of a substance is the free energy change of the reaction by which this substance is obtained from its constituents. A positive free energy indicates that a substance is unstable and tends to decompose.

It may be shown that the free energy change ΔF and the equilibrium constant K of any chemical reaction are related by the very important equation.

$$\Delta F = - RT \ln K, \qquad (13)$$

T being the temperature.[8] This relation brings out several important facts.

In the first place, as K is a function of the temperature (equation 1), ΔF must be a function of the temperature also. On the other hand, as K depends on the concentrations of the reactants and products at equilibrium ΔF depends on these concentrations also. For instance, if equilibrium is reached when reactants and products are at unit activity,[9] $K = 1$, and $\Delta F = 0$. If $\Delta F < 0$, there is a tendency for the reactants, at unit activity, to give the products, at unit activity; if $\Delta F > 0$, *i.e.*, if the system is in a state of equilibrium when the activities of the products are less than those of the reactants, the reactions will go in the reverse direction.

[8] A demonstration of this relation may be found in any text book on physical chemistry. See, for instance, Getman and Daniels: Outlines of theoretical chemistry, 5th edit., p. 271, 1931.

[9] Activities are effective concentrations, *i.e.*, quantities such that the mass action law and the laws of the thermodynamics may be applied with exactness when they are substituted for concentrations. The activity is equal to the molal concentration multiplied by a coefficient called the activity coefficient. This activity coefficient may be determined experimentally by several methods.

FREE ENERGY AND SOLUBILITY PRODUCT.

Consider the reaction

$$Zn^{++} + S^{=} \rightleftarrows ZnS_{sol}.$$

If K is the equilibrium constant of this reaction, since ZnS_{sol} is at unit activity, it follows from the definition of the solubility product P that $P = 1/K$, or, according to (13),

$$\Delta F = - RT \ln 1/P. \qquad (14)$$

Equation (14) is the wanted relation between free energy and solubility product.

The following example may illustrate equation (14).

According to definitions, the free energy change of the reaction $Zn^{++} + S^{=} \rightleftarrows ZnS$ is the difference between the free energies of products and reactants:

$$\Delta F = F_{ZnS} - (F_{Zn^{++}} + F_{S^{=}}). \qquad (15)$$

$- F_{ZnS}$, the free energy of formation of zinc sulphide, is 46,900 cal., according to Ravitz.[10] $F_{Zn^{++}}$ and $F_{S^{=}}$ may be computed from (12) where the normal potentials of zinc and sulphur are substituted for E. Equation (15) becomes

$$\Delta F = - 46{,}900 - (- 2 \times 23{,}060 \times 0.761 + 2 \times 23{,}060 \times 0.51)$$
$$= - 35{,}250 \text{ cal.}$$

Substituting in (14)

$$\ln 1/P = \frac{35{,}250}{1.98 \times 298},$$

all data being given at 25° C.

Solving for P:

$$P = 1.15\ 10^{-26},$$

which is the value given by Ravitz (Table I).

The solubility product may be calculated by the same method at any temperature, provided the free energies of the sulphide and of its ions are known at that same temperature.

[10] Jour. Phys. Chem., vol. 40, pp. 61–70, 1936.

INFLUENCE OF TEMPERATURE ON FREE ENERGY CHANGE.

Dividing both sides of equation (13) by T and differentiating with respect to T, it comes

$$\partial \frac{\frac{\Delta F}{T}}{\partial T} = -\frac{\partial \ln K}{\partial T}.$$

Since

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H}{RT^2} \tag{1}$$

it follows that

$$\partial \frac{\frac{\Delta F}{T}}{\partial T} = -\frac{\Delta H}{T^2}. \tag{16}$$

ΔH is a function of the temperature and obeys the well-known Kirchhoff's law:

$$\Delta H = \Delta H_0 + \int_0^T \Delta c_p dT, \tag{17}$$

where ΔH_0 is a constant and Δc_p is the difference between the heat capacity of the products and the reactants. The heat capacity of a substance may be expressed as a function of the temperature by the relation

$$c_p = a + bT, \tag{18}$$

a and b being constants. Integrating (17), it comes

$$\Delta H = \Delta H_0 + \Delta a T + \Delta b T^2/2, \tag{19}$$

Δa and Δb being the differences between the constants a and b of the products and the reactants. ΔH_0 must be determined from the knowledge of ΔH at any one temperature.

Substituting in (16) and integrating once more:

$$\Delta F = \Delta H_0 - \Delta a T \ln T - \Delta b T^2/2 + IT, \tag{20}$$

I being an integration constant which must be determined from ΔF at any one temperature.

This equation may be illustrated as follows: the heat capacities

of sulphur, zinc, and zinc sulphide, may be represented by the following equations:

$$\begin{aligned} c_{p,S} &= 4{,}12 + 0.0047T, \\ c_{p,Zn} &= 5.10 + 0.003T, \\ c_{p,ZnS} &= 10.80 + 0.0012T,^{11} \\ \Delta c_p &= 1.58 - 0.0065T. \end{aligned}$$

At 298° K., $\Delta H = -48{,}355$ cal. Substituting these numerical values in (19)

$$\begin{aligned} \Delta H_0 &= -48{,}355 - 1.58 \times 298 + 0.0065 \frac{298^2}{2} \\ &= -48{,}538 \text{ cal.} \end{aligned}$$

At 298° K., $F_{ZnS} = -46{,}900$ cal. Thus, from (20)

$$-46{,}900 = -48{,}538 - 1.58 \times 298 \times \ln 298 + \tfrac{1}{2}\, 0.0065 \times 298^2 + 298I$$

or

$$I = +13.5.$$

The free energy of zinc sulphide may accordingly be calculated at any temperature by the relation

$$F_{ZnS} = -48{,}538 - 1.58T \ln T + 0.00325T^2 + 13.5T.$$

The following equations have been obtained by the same method: [12]

$$\begin{aligned} F_{PbS} &= -22{,}400 - 1.85T \ln T + 0.0028T^2 + 11.1T, \\ F_{CuS} &= -12{,}120 - 2.45T \ln T + 0.0025T^2 + 14.02T, \\ F_{HgS} &= -10{,}595 - 0.07T \ln T + 0.003\ T^2 + 23.8T, \\ F_{Ag2S} &= -\ 4{,}318 + 4.87T \ln T - 0.0087T^2 - 41.8T, \\ F_{Cu2S\alpha} &= -17{,}920 + 8{,}29T \ln T - 0.016\ T^2 - 46.46T, \\ F_{Cu2S\beta} &= -20{,}440 - 5.41T \ln T - 0.0037T^2 + 36.86T. \end{aligned}$$

Numerical values of these functions at 25° C., 100° C., 200° C., 300° C., and 400° C., are given in the appended table.

[11] International Critical Tables, 1931.

[12] Equations for CuS, Cu_2S_α, and Cu_2S_β are taken from the International Critical Tables (vol. 7, p. 263, 1931).

TABLE III.

FREE ENERGY OF FORMATION OF SULPHIDES.[13]

	25°	100°	200°	300°	400°
ZnS	− 46,900	− 46,548	− 46,032	− 45,461	− 44,980
PbS	− 21,977	− 21,946	− 21,908	− 21,850	− 21,760
CuS	− 11,755	− 11,933	− 12,060	− 12,150	− 12,238
HgS	− 3,350	− 1,462	+ 1,123	+ 3,765	+ 6,461
Ag_2S	− 9,930	− 10,357	− 11,844	− 13,393	− 15,072
Cu_2S_α	− 19,110	− 19,160	− 19,260	− 19,610	− 20,050
Cu_2S_β	− 18,970	− 19,155	− 19,576	− 20,234	− 20,980

It may be noticed that the free energy of HgS changes sign, becoming positive between 100° and 200°. This means that at higher temperature, HgS is unstable and tends to decompose.

Regarding the stability of Cu_2S_α and Cu_2S_β, figures in Table III indicate that the free energies of these two forms become approximately equal at 100°, meaning that the inversion temperature is close to this temperature (actual inversion temperature: 103° C., according to the I. C. T., from which these data have been compiled). Above 103°, Cu_2S_β becomes stable, as indicated by its free energy which is greater than, and of the same negative sign as, the free energy of Cu_2S_α.

The free energies of the sulphides being known, it becomes necessary to calculate the free energies of the ions, as shown by equations (14) and (15). Account must be taken of the fact that the normal potential E changes with temperature according to the relation

$$E + \frac{\Delta H_i}{n \times 96{,}500} = T\frac{dE}{dT}, \qquad (21)$$

where ΔH_i is the heat of ionization and dE/dT is the wanted temperature coefficient of the normal potential. Equation (21) may be readily verified by (12) and (16).

The heat of ionization ΔH_i of the elements may be found in any table of constants,[14] or may be calculated from the heat of formation and the heat of solution of simple substances. Values of E are also

[13] Data at 25° C., excepted for Cu_2S, are compiled from Ravitz (op. cit.).

[14] Intern. Crit. Tables, vol. 5, p. 186, 1931.

to be found in tables, so that dE/dT may be readily calculated, as well as values of the normal potential at 100° C., 200° C., etc. The corresponding values of the free energy of the ions, computed from (12), are then substituted in equations similar to (15), together with the free energies of the sulphides listed in Table III. ΔF being known from (15), the solubility product P may be easily calculated by equation (14), as illustrated above for zinc sulphide.

Results of these calculations have been summarized in the appended table.

TABLE IV.

SOLUBILITY PRODUCT OF SULPHIDES, UP TO 400° C.[15]

	25°	100°	200°	300°	400°
ZnS	$1.15\ 10^{-26}$	$4.16\ 10^{-20}$	$5.50\ 10^{-15}$	$1.56\ 10^{-11}$	$1.31\ 10^{-9}$
FbS	$7.00\ 10^{-30}$	$4.35\ 10^{-27}$	$7.95\ 10^{-24}$	$9.80\ 10^{-22}$	$2.82\ 10^{-20}$
CuS	$3.48\ 10^{-38}$	$5.62\ 10^{-37}$	$2.51\ 10^{-34}$	$1.26\ 10^{-32}$	$2.50\ 10^{-31}$
HgS	$1.00\ 10^{-47}$	$2.80\ 10^{-46}$	$7.95\ 10^{-43}$	$1.26\ 10^{-40}$	$6.16\ 10^{-39}$
Ag_2S	$3.28\ 10^{-52}$	$6.34\ 10^{-51}$	$3.96\ 10^{-48}$	$5.62\ 10^{-46}$	$5.00\ 10^{-45}$
Cu_2S_α	$2.50\ 10^{-42}$	$8.00\ 10^{-45}$			
Cu_2S_β		$8.00\ 10^{-45}$	$7.10\ 10^{-41}$	$1.60\ 10^{-38}$	$6.14\ 10^{-37}$

The numerical data in table IV may now be substituted in equations (6) and (7). Taking into account that K_1 and K_2 change with temperature according to (1),[16] the following have been obtained (Table V):

[15] Values at 25°, excepted for Cu_2S, are reproduced from Table I.

[16] The heat of reaction of (5) is given as + 6,000 cal. (Lewis and Randall, op. cit., p. 543). That of reaction (4) is not known, but may be calculated as follows:

$$H_2S \rightleftarrows H^+ + HS^- \qquad H = +6{,}000 \text{ cal. (5)}$$
$$H_2S \rightleftarrows 2H^+ + S^= \qquad H = +9{,}869 \text{ cal. (L. and R., op. cit., p. 543).}$$

Thus

$$HS^- \rightleftarrows H^+ + S^= \qquad H = +3{,}869 \text{ cal. (4).}$$

Values of K_1 and K_2 at 100°, 200°, etc., may now be calculated by use of the integrated form of equation (1) and are given below:

T°	K_1	K_2
25° C.	10^{-15}	$1.15\ 10^{-7}$
100° C.	$3.74\ 10^{-15}$	$4.45\ 10^{-7}$
200° C.	$1.13\ 10^{-14}$	$1.00\ 10^{-6}$
300° C.	$2.34\ 10^{-14}$	$1.70\ 10^{-6}$
400° C.	$3.88\ 10^{-14}$	$2.50\ 10^{-6}$

TABLE V.

SOLUBILITY OF SULPHIDES, UP TO 400° C. (GMS. PER LITER).[17]

	ZnS	PbS	CuS	HgS	Ag_2S	Cu_2S	
25° C.	$1.42\ 10^{-7}$	$8.65\ 10^{-9}$	$2.4\ 10^{-13}$	$1.0\ 10^{-18}$	$3.8\ 10^{-13}$	$4.8\ 10^{-10}$	$Cu_2\alpha$
100° C.	$3.6\ 10^{-4}$	$8.9\ 10^{-8}$	$4.1\ 10^{-12}$	$2.2\ 10^{-17}$	$5.7\ 10^{-13}$	$4.0\ 10^{-11}$	$Cu_2\alpha$
200° C.	$2.2\ 10^{-2}$	$2.1\ 10^{-6}$	$4.6\ 10^{-12}$	$6.4\ 10^{-16}$	$3.3\ 10^{-12}$	$5.6\ 10^{-10}$	$Cu_2S\beta$
300° C.	0.8	$1.6\ 10^{-5}$	$2.3\ 10^{-11}$	$5.6\ 10^{-15}$	$1.4\ 10^{-11}$	$2.6\ 10^{-9}$	$Cu_2S\beta$
400° C.	5.92	$2.1\ 10^{-4}$	$7.8\ 10^{-11}$	$3.1\ 10^{-14}$	$2.3\ 10^{-11}$	$7.3\ 10^{-9}$	$Cu_2S\beta$

These results have been plotted on a logarithmic scale in Fig. 2. The fact that errors of, say, 500 calories on the free energies could hardly change the order of magnitude of the solubilities may be sufficient, to the accuracy aimed at by geologists, to warrant the assumptions that have been made, namely,

(1) that the specific heats change with temperature according to equation (18);
(2) that dE/dT remains constant throughout the temperature range 25° − 400° C.;
(3) that the pressure required to prevent the solution from boiling off has no effect on the solubility.

Calculations have not been carried out beyond 400° C., as data on specific heats of sulphides are not available above this temperature. It is felt, however, that the curves in Fig. 2 could be safely extrapolated to 500°, at least for those sulphides with a high melting point. It remains to be seen whether solubilities at temperatures much above 500° C. would be of any geological significance.

DISCUSSION OF RESULTS.

The solubility curves plotted in Fig. 2 bring out the interesting fact that, with the exception of the Ag_2S − CuS reversal, the order of increasing solubility remains the same at 400° as at 25° C. This may throw light on the much vexed question of zonal deposition. The fact that the less soluble sulphides are commonly found to have left the magma later, and to have been deposited farther away, than the more soluble ones, has led, together with other theoretical con-

[17] Calculated for a solution of pH = 7. Because of the increased dissociation of water, a solution of pH = 7, at 400° C., would be slightly alkaline.

siderations, to the suggestion that the order of increasing solubilities might be reversed at high temperature.[18] This hypothesis is not met below 400° C., and from the shape of the curves in Fig. 2, it is

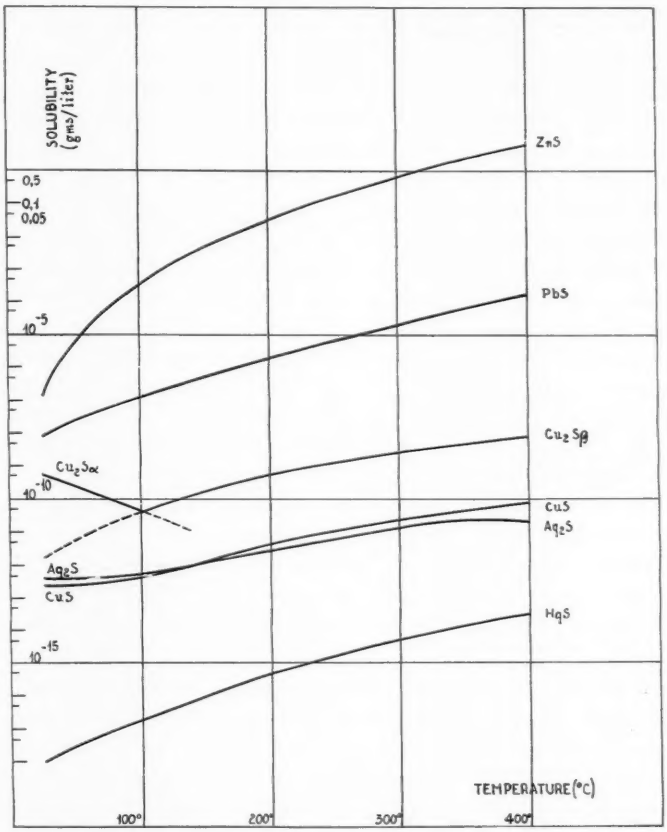


FIG. 2.

doubtful whether any such reversal takes place within the range of hydrothermal or pneumatolytic deposition. What may happen at temperatures near the melting point of the sulphides remains, of

[18] de Magnée, I.: Ann. Soc. Geol. Belg., vol. 55, pp. M9–35, 1932.

course, a matter for speculation. It is probable, however, that close to the melting point the solution, or rather the melt, would contain but a few percent of water, and conditions would obtain that could hardly be considered to have prevailed during the deposition of ore bodies other than orthomagmatic ones.

The fact that solubility data seem inadequate to explain the zonal disposition of sulphides, as the less soluble sulphides would be expected to precipitate closer to the magma, may lend support to the view that the orthomagmatic, high temperature, part of the sulphide-water diagram is the important one, the metals leaving the magma in a well-defined order, connected perhaps to the order of increasing entropy of fusion of the sulphides.[19] It is scarcely probable that the metals should be transported as sulphides in a vapor phase, as there seems to be no visible connexion between the usual sequence of deposition and the order of increasing vapor pressure of the sulphides,[20] in contrast to the remarkable analogy between this sequence and the order of increasing solubility products.[21] Possibly, the initial concentrations of the metals in the magma are of greater importance in determining the course of events than is commonly acknowledged.

Attention should be paid to the shape of the curves in Fig. 2, as the slope of these curves seems to be greater for the more soluble sulphides than for the less soluble ones. This means that for equal changes in temperature, proportionally greater amounts of the more soluble sulphides will be precipitated from their saturated solution.

It does not seem likely that the problem of zonal deposition could be solved until more experimental data have been supplied. There is much need for thermal data on sulphides, and it is highly desirable that information should be obtained concerning those sulphides for which free energies, solubility at 25°, etc., are not known. Pending the completion of these much required experimental determinations,

[19] As this entropy of fusion determines, in the neighborhood of the melting point of the sulphide the lowering of the freezing-point of the system water-sulphide (Austin, J. B.: Jour. Am. Chem. Soc., vol. 57, p. 2428, 1935).

[20] Kordes, E.: Min. Petr. Mitt., vol. 46, p. 256, 1935.

[21] Lindgren, W.: Mineral Deposits, p. 123, New York, 1933.

this paper is offered in the hope that it may be useful to those interested in problems of ore deposition.

ACKNOWLEDGMENT.

The writer wishes to acknowledge help from Dr. Van Ryssel-berghe, of the Chemistry Department of Stanford University, who has kindly developed the method for calculating solubilities from solubility products. Prof. de Magnée has made valuable suggestions and kindly criticized this paper.

UNIVERSITY OF BRUSSELS,
BRUSSELS, BELGIUM,
October 20, 1937.

SOME MINERAL DEPOSITS OF GLACIER BAY AND VICINITY, ALASKA.[1]

JOHN C. REED.

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ABSTRACT.

Prospecting in the Glacier Bay National Monument has been confined so far to granitic rocks near contacts with Paleozoic sediments, which they intrude.

Near Reid Glacier thin veins, a few of which are traceable for about 300 feet both horizontally and vertically, trend northerly and carry sphalerite, galena, and pyrite. Gold was panned from some of the better looking material.

Near Sandy Cove, 30 miles away, more irregular, but locally

[1] Published by permission of the Director, U. S. Geological Survey. Presented before the Society of Economic Geologists, New York Meeting, February, 1937.

thicker, veins appear to carry only pyrite. Here pyrite also occurs along the contact between the granitic rocks and the intruded limestone.

Sparse ore minerals have been seen at other places in and near the monument. As yet, no large mineral deposits have been found there, but many miles of igneous contacts have not been prospected. In southeastern Alaska, as elsewhere, such contacts are considered favorable places in which to search for mineral deposits.

INTRODUCTION.

GLACIER BAY is in the northwest part of southeastern Alaska (Fig. 1).

The entrance to Glacier Bay is about 60 miles west of Juneau from which place it is reached by plane or boat.

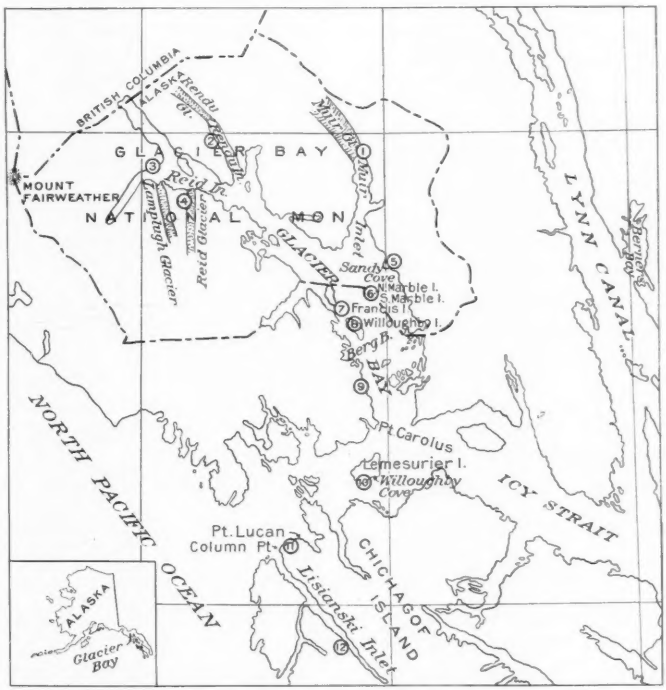

FIG. 1. Outline map of Glacier Bay and vicinity, Alaska, showing locations of some mineral deposits.

Glacier Bay has been visited by several geological expeditions but most of these were principally concerned with the study of glacial phenomena that are well displayed there. Greatly increased interest, because of the recent opening of the Glacier Bay National Monument to prospecting and mining, in the economic possibilities of the mineral deposits of Glacier Bay resulted in their investigation by the United States Geological Survey during a 4-week period in August, 1936.

The investigation included the examination of most of the known deposits of metallic minerals in the Glacier Bay district as well as brief visits to a few deposits south of there on Lemesurier Island in Icy Strait, and on Chichagof Island.

Most of the deposits examined do not appear to be of very great commercial importance. A few may have some commercial possibilities but have not yet been prospected sufficiently to permit safe appraisal. Two formerly productive mines were visited, the Apex and the El Nido on Chichagof Island. The deposits at these mines are more developed than those seen at any of the other places.

Most of the deposits visited appear to be genetically related to bodies of granitic rock. Because many of these granitic masses, and particularly their contacts against older rocks have not been explored geologically, even in a reconnaissance way, a general statement that the area either is or is not one in which commercial ore bodies are likely to occur is probably not yet warranted.

In this paper a short outline of the general geology of the area is followed by descriptions of the deposits examined, and by a summary of some of their outstanding geological features.

GEOLOGIC SETTING.

The area in which the deposits visited lie is one of limestone and marble, probably of Upper Silurian age, and other sediments including argillite, slate, quartzite, and hornfels, that also are probably Silurian or older. The sediments were intruded probably in Upper Jurassic or Lower Cretaceous time by many dif-

ferent-sized, irregularly shaped masses of granitic rocks, principally diorite.

Along Lynn Canal is exposed a group of sedimentary rocks younger than those around Glacier Bay. Most of the rocks of the group are probably Jurassic or Cretaceous but some of them may be Triassic and others Paleozoic. The principal types represented are slate and graywacke with some greenstone.

The principal bed rocks of Glacier Bay and vicinity are cut at many places by a variety of dike rocks including pegmatites, aplites, and lamprophyres; the last are the most abundant. The pegmatites and aplites are regarded as being genetically related to the diorite intrusions but the lamprophyres are probably much younger.

Large areas of the bed rocks are concealed beneath unconsolidated Quaternary fluviatile and glacial deposits and still larger areas are covered by snow and ice fields and by active glaciers.

The general structural trend in the northern part of southeastern Alaska is northwest. At most places the dip is steep. Apparently the magmas, which upon crystallization formed the granitic bodies, were more readily intruded along the pre-existing structural trend than across it and many of the bodies, particularly the larger ones, are elongated in that direction.

According to Buddington and Chapin [2] the belt of rocks east of the Glacier Bay district along Lynn Canal is part of the Juneau synclinorium whereas the rocks of the north end of Chichagof Island and Glacier Bay comprise part of the Chichagof-Glacier Bay anticlinorium.

F. E. and C. W. Wright [3] believe that Lynn Canal and Chatham Strait have been eroded along a major fault plane that trends slightly west of north.

DESCRIPTIONS OF DEPOSITS AND LOCALITIES.

The numbers in parentheses after the following paragraph headings correspond to the locality numbers on Fig. 1.

[2] Buddington, A. F., and Chapin, Theodore: Geology and mineral deposits of southeastern Alaska. U. S. Geol. Surv. Bull. 800, pp. 298 and 315, 1929.

[3] Wright, F. E. and C. W.: The Glacier Bay National Monument in southeastern Alaska, its glaciers and geology. U. S. Geol. Surv. unpublished manuscript.

Head of Muir Inlet (1).

A small mountain, 1,150 feet high by aneroid barometer, rises near the head of Muir Inlet on the east side of the main Muir Glacier and between it and a large area of stagnant ice farther east. The country rock is principally hornfels; its general strike is N. 40° E. and its dip about 50° N.W. Two varieties of hornfels are distinguished by color differences, one is composed of bands, many less than an inch thick, of nearly white and light gray or buff rock; the other is much darker and may be either dark green or gray.

The light colored hornfels is made up principally of crushed quartz grains and variable amounts of zoisite. Some rounded and strained quartz nuclei are present in the ground mass of more finely crushed material. Some of the bands carry needles of pale green amphibole. Pyrrhotite, pyrite, and possibly chalcopyrite are accessory minerals. The rock is cut by tiny seams of coarser-grained quartz and zoisite.

The darker hornfels is so fine grained that the principal mineral constituents are determined with difficulty even with the microscope. Apparently quartz is the most abundant mineral. In other respects the rock is similar to the lighter variety except that green amphibole is more abundant and zoisite less abundant. The amphibole is probably responsible for the darker color of this variety of the hornfels.

Granitic dikes up to more than 100 feet thick are common in the hornfels and are particularly abundant near the top of the mountain. The rock of the dikes is porphyritic quartz diorite. The plagioclase phenocrysts appear to range from oligoclase to andesine whereas the ground-mass feldspars are albite or oligoclase. The dark minerals have been altered to serpentine but the shapes of the serpentine masses indicate that the principal original dark mineral probably was hornblende. Pyrite, apatite, and birefringent garnet are accessories.

Small mineralized quartz veins are, like the quartz diorite dikes, more abundant near the top of the mountain. The veins are apparently confined to the hornfels and were not seen in the

dikes. None of the veins observed is more than 6 inches thick. Many of them strike N. 70° W. and are vertical. Some trend in other directions.

The mineralogy of the quartz veins has not yet been studied in detail. The principal metallic minerals appear to be magnetite and chalcopyrite in an intimate mixture. Pyrite is not abundant. Some other minerals are known to be present, among them one that appears creamy-white when polished, isotropic, soft, and shows reddish internal reflections around its borders. Possibly it is ruby silver.

Although the mountain appeared as a nunatak through the ice of Muir Glacier less than 50 years ago, the sulphides are partly oxidized where the veins outcrop. Hydrated oxides of iron, chrysocolla, malachite, and possibly cuprite are common.

West Side of Rendu Inlet (2).

According to Buddington's unpublished notes,[4] 2 claims [5] on the west side of Rendu Inlet were patented about 1892. Tetrahedrite is reported to have been found on them. An attempt to identify the claims with certainty proved unsuccessful. A rock monument found along the shore about three miles down the inlet from Rendu Glacier may represent the location of the claims.

The country rock in the general vicinity is quartz diorite, which appears very similar to the granite near Reid Glacier (4). It is composed principally of quartz, oligoclase-andesine, and pale green amphibole. It contains some orthoclase and biotite and carries accessory calcite, sericite, chlorite, epidote, zoisite, apatite, and magnetite.

At most places seen the quartz diorite contains many different-sized lenticular inclusions of a finer grained, darker colored, porphyritic rock. Mineralogically and texturally the inclusions resemble lamprophyre. The most abundant mineral is oligoclase. Many of the oligoclase crystals are lath-shaped and untwinned. Blunt laths of light green amphibole are abundant. A little

[4] Buddington, A. F.: U. S. Geol. Surv. unpublished notes, 1924.

[5] Reported to belong to the Presbyterian Home for Elders in Seattle.

chlorite, apparently at least in part after biotite, magnetite, apatite, calcite, and epidote were also recognized.

The country rock is cut at a few places by light colored dikes. Several altered zones, which contain tiny mineralized quartz veinlets, were observed. These appear similar to the altered zones with quartz veins near Reid Glacier (4) but are not as wide, as continuous, or as numerous.

North Shore of Reid Inlet (3).

In a contact zone along the north shore of Reid Inlet, from a point across the inlet from Lamplugh Glacier, for several miles westward to about the sharp bend whence the inlet trends southwestward, a large granitic mass on the east gives way to a thick sequence of limestone and slate that appears to occupy a considerable area to the west. An abundant rock of this zone is dark gray, blocky slate that is composed largely of quartz and feldspar grains that form a fine-grained ground mass in which are numerous large, broken grains of the same minerals. Carbonaceous material is common and pyrite and zoisite are present. The rock is traversed by a few thin calcite seams. Another common rock is calcareous green slate. Some bands are made up of quartz in broken grains and calcite. Other bands are shaly. Zoisite is common.

Throughout this zone, different-sized masses of the sediments lie out in the granitic rock. The strike at most places in the zone is between N. 40° W. and N. 55° W. and the dip between 60° and 75° S.W.

Locally the sediments of the engulfed masses of the contact zone are replaced by bodies of massive pyrite. The largest such deposit seen is about 10 feet thick at the water line but thins to about a foot about 50 feet above the water. This deposit can be traced by eye, because of the conspicuous staining by hydrated oxides of iron, for a long distance up the fiord wall.

Some quartz and a very little chalcopyrite are present in the massive pyrite. An estimate of the percentages of pyrite, quartz, and chalcopyrite in the most completely replaced material in 95, 5,

and less that 1, in the order given. The precious metal content of this material, if any, is not known.

Reid Glacier (4).

J. P. Ibach staked for himself and associates 2 claims in 1924 and many more in the summer of 1936 in the vicinity of Reid Glacier. One group of claims lies west of the glacier and near the ice front. Another group is on the east side of the glacier, and a third is almost on the divide between Reid and Lamplugh Glaciers. These claims have been prospected very slightly and have had no production.

Claims West of Reid Glacier near the Ice Front.

The claims west of Reid Glacier include the Galena and other groups. Fig. 2 is a map of some of the geographic and geologic features of the vicinity.

Rocks.—The principal country rock of the area mapped appears to be granite. The granite contains different-sized masses of engulfed older sediments which are siliceous and possibly originally were sandstones. Marble and slate crop out along the east side of Reid Glacier and on the divide between Reid and Lamplugh Glaciers about a mile south of the mapped area. The granite and older rocks are cut by dark colored dikes including many of lamprophyre and perhaps some of other rocks.

The designation of the intrusive rock as granite is based on the study of one thin section only, but the rock from which the section was cut appears to be typical. The section is made up principally of orthoclase and albite-oligoclase. Quartz is present in considerable quantity. The original dark minerals have been converted to chlorite and other alteration products. The shapes of the chlorite masses in the hand specimen indicate the former presence of hornblende and possibly of some biotite. Accessory minerals include epidote, titanite, and apatite.

The different-sized masses of light colored, cherty-appearing rock that is thought to have been sandstone is made up of a mosaic of angular quartz grains. The grains are crushed around their

edges and most of them are cracked and strained. The grains are partly altered to sericite which has developed in the quartz according to an unusual reticulate pattern. The quartz mosaic is

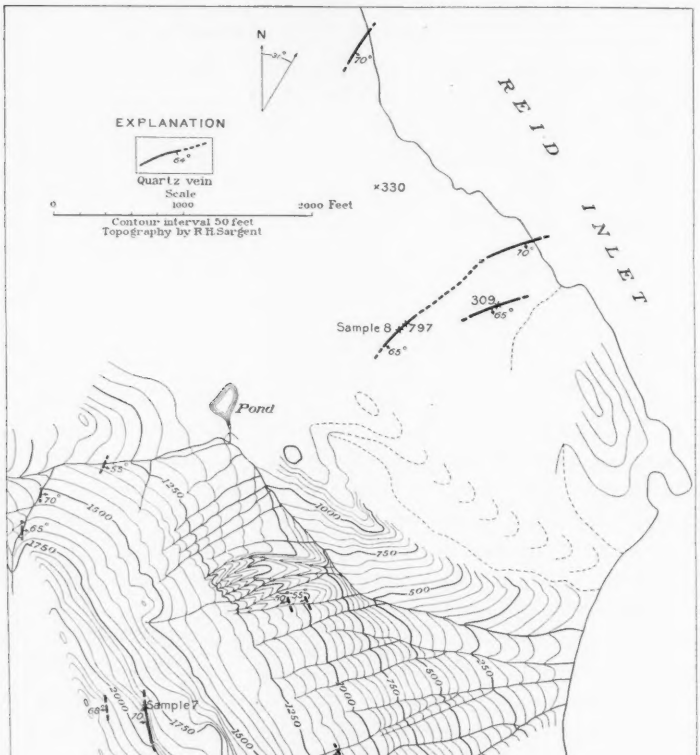

FIG. 2. Map, showing quartz veins, of an area west of Read Glacier near the ice front.

cut by numerous intersecting quartz veinlets that are free of sericite. Calcite is sparingly present in the veinlets. Pyrite is a common accessory of both the veinlets and the main mass of the rock.

The most abundant mineral of the lamprophyre dikes is plagioclase, which is either calcic albite or sodic oligoclase. The dark mineral is pale green hornblende which in many places is partly altered to chlorite and other products. Accessories include calcite, epidote, magnetite, pyrite, and sericite.

The sedimentary rocks east of Reid Glacier and those south of the small mapped area trend in general northwest but locally the strikes diverge from that direction. There appears to be no consistency of dip. No directional features reflecting the general structural trend of the older rocks were observed in the granite. The engulfed quartzite masses are too irregular and poorly exposed to indicate the structure by their shapes and attitudes, and the rock is metamorphosed to such a degree that bedding has been obliterated.

Most of the lamprophyre dikes in the granite trend about E. and dip steeply, ordinarily more than 70 degrees, either N. or S. The dikes of this group are larger, more abundant, and older than lithologically similar dikes that strike in general about N. 15° E. and dip between 65° W. and vertical. The range of strikes of 6 dikes of the latter group is from N. 5° W. to N. 35° E. (Fig. 3).

Veins.—The bed rocks of the mapped area and vicinity are cut by quartz veins that range in thickness from a small fraction of an inch to as much as 18 inches. Several of the veins were traced horizontally for about 400 feet and for about the same distance vertically. One, with some interpolation, is mapped for a horizontal distance of about 1600 feet and over a vertical range of more than 800 feet (Fig. 2).

Most of the veins range in strike from N. 25° W. to N. 57° E. and have steep dips (Fig. 3). The veins appear to fill fractures of the same group as those occupied by the later lamprophyre dikes.

The granite of the country rock is commonly intensely altered for several feet on each side of a vein. In several places fractures were observed along which alteration has taken place but which contained no vein. Locally several thin veinlets occupy

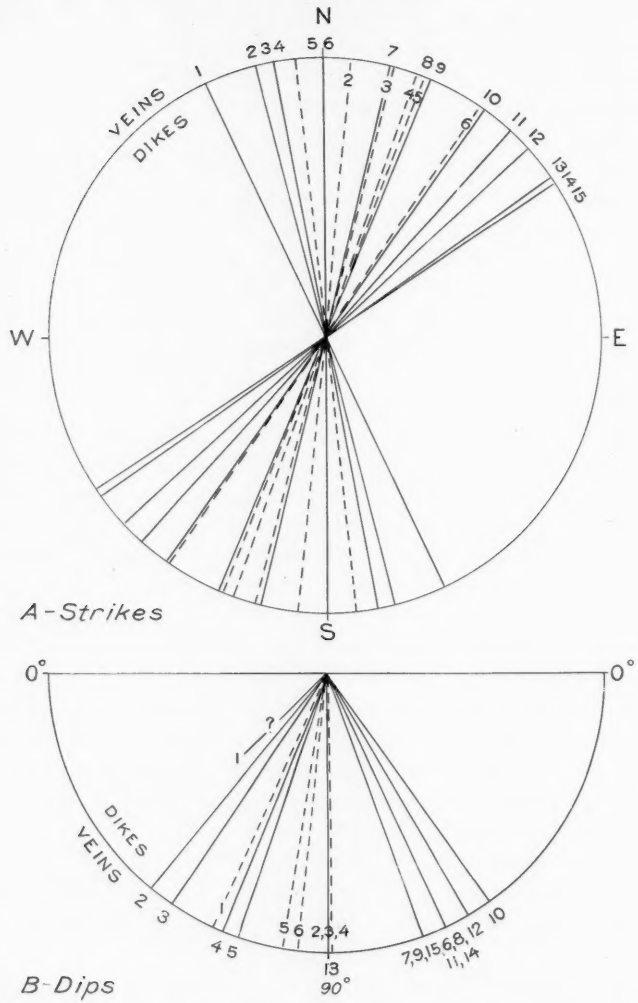

FIG. 3. Diagram showing attitudes of veins and of younger lamprophyre dikes near Reid Glacier.

single fracture zones. The altered zones are apparent in the field because of their conspicuous bright color due to hydrated oxides of iron. The principal changes in the rock by the alteration are the addition of a great deal of quartz, the destruction of all of the hornblende, most of the orthoclase, and part of the plagioclase, and the formation of considerable calcite, sericite, and pyrite. Many of the altered zones are 20 feet thick and few are less than 10 feet.

The quartz of the veins is commonly banded, with comb quartz and vugs near the centers. The walls are free and are locally marked by a little gouge. Ore minerals observed include pyrite, marcasite, sphalerite, galena, and chalcopyrite. Of these, pyrite and sphalerite are the most abundant. The deposition of the ore minerals appears to have been partly controlled by the banding of the vein, for the metallic minerals are largely confined to thin zones between bands. The sphalerite and galena are more abundant in the comb quartz of the interiors of the veins whereas the pyrite appears to be distributed through all the quartz.

Not much is known about the precious metal content of the veins as they have never been adequately sampled. Free gold, some of it coarse, was panned from some of the richer looking vein material. A sample cut from a vein 12 inches wide that outcrops a short distance south of the mapped area at an altitude of about 340 feet yielded[6] 0.16 oz. gold, 0.30 oz. silver and 0.79% zinc per ton. Two other samples (No. 7, 18 inches wide and No. 8, 6 inches wide) cut from veins within the mapped area (Fig. 2) yielded the following results:

No.	Gold, oz.	Silver, oz.	Zinc, per cent.
7	0.97	0.50	1.08
8	0.84	0.10	1.02

[6] All assays, unless otherwise noted, by W. T. Burns, U. S. Geological Survey, Fairbanks, Alaska.

Claims East of Reid Glacier.

The Sunrise group of 10 claims lies along the east side of Reid Glacier and extends north of the ice front for several thousand feet.

Here white marble, bluish marble, and dark green, blocky slate are cut by numerous lamprophyre dikes similar to those described from the west side of Reid Glacier. The metamorphic rocks strike from about N. 20° W. to N. 15° E. The general dip along the glacier and the inlet in front of it is about 55° E. but a short distance to the east the beds dip west.

The lamprophyre dikes and a few small quartz veins are about parallel to the beds. The dikes range up to 30 feet thick, and in places are bordered by a silicious contact rock. A thin section of this is composed largely of quartz grains. About 20 per cent of the section is pinkish-brown mica, and it contains considerable plagioclase (mostly untwinned), which ranges from albite to sodic andesine. Apatite is a common accessory as is zoisite, which is present in veinlets cutting the other minerals. A polished section of the same rock reveals about 15 percent sulphides among which pyrrhotite, pyrite, and arsenopyrite were recognized. Of these the first is the most abundant. At other places along dike contacts are small irregular patches and kidneys of sulphides in calcite, none of which are more than a few inches in diameter; they contain chalcopyrite and pyrrhotite.

The quartz veins of this vicinity are small and discontinuous. None was traced definitely for more than a few tens of feet. One vein that, where observed, ranges in thickness from 2 inches to 18 inches was sampled where it is 10 inches thick, and yielded 0.08 oz. in gold and 0.20 oz. in silver per ton. Some of the sedimentary material under the vein that was sampled carries sulphides, possibly pyrrhotite, and was reported to contain considerable gold. An assay of this material from about 6 feet under the vein showed a trace of both gold and silver.

Claims Near the Divide between Reid and Lamplugh Glaciers.

The Rambler Group of 6 claims lies about 2 miles southwest of the front of Reid Glacier near the divide between Reid and Lamplugh Glaciers at an altitude of about 2,850 feet.

The mineral showing here is in the same granitic body as those farther north in the vicinity of the front of the glacier. Marble and other rocks crop out a few hundred feet west of the prospect and on the divide north of the prospect. The marble strikes about N. 50° W. and dips about 50° S.W. The typical marble is interbanded dark, impure layers and white, coarsely crystalline layers, which range from about 0.01 to 0.5 inch in thickness. The rock is principally composed of large calcite crystals in a mosaic of finer calcite grains. Small quantities of muscovite, colorless pyroxene, colorless amphibole, quartz, feldspar, and a sulphide, apparently pyrrhotite, are present.

At the discovery, the granitic rock is cut by a zone of intensely altered rock about 20 feet thick, which consists mostly of quartz and calcite. The quartz is greatly strained and locally crushed. Only a little plagioclase is left; it appears to be oligoclase but is so sericitized that its determination was difficult. The rock contains considerable pyrite. The altered zone strikes about N. 10° E. and dips 70° W. To the south, the zone passes under a small glacier and was not found beyond. On the north it appears to split into a large number of smaller zones that are shortly lost in the country rock. In the zone are 4 or 5 parallel quartz veinlets. The largest seen is locally about 2 feet thick. The quartz is vuggy and the vein carries pyrite, sphalerite, and galena.

A sample of typical vein material yielded 0.26 oz. gold and 0.10 oz. silver per ton, and the rock of the altered zone yielded a trace of gold and 0.20 oz. of silver to the ton.

Sandy Cove (5)

Three claims near Sandy Cove on the east side of Glacier Bay are held by the Glacier Bay Mining Co. of Frank St. Clair, Edward Metjay, James Austin, and Wm. L. Paul. The principal development consists of a tunnel which was about 30 feet long

when the property was visited but which was reported in March 1937, to be a little more than 100 feet long. A small compressor, and some other mining equipment are on the property.

Here, a small body of granitic rock intrudes thick-bedded limestone now largely crystallized to marble (Fig. 4). A thin section

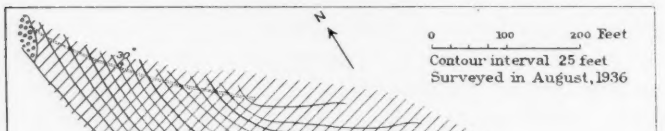

FIG. 4. Topographic and geologic map of vicinity of prospect of the Glacier Bay Mining Co.

of typical granitic rock shows it to be monzonite. It is composed principally of oligoclase, orthoclase, and pale green amphibole. A little quartz is present as well as small quantities of epidote, zoisite, calcite, sericite, and garnet. Pyrite and titanite are common.

At most places the thick-bedded limestone is bluish gray, locally it is coarsely crystalline white marble, and at a few places the rock is stained brown or red by hydrated oxides of iron. At many places along and near the contact between the monzonite and the limestone and in some zones within the limestone, possibly along

certain beds, the limestone has been changed by contact metamorphism into complex rocks largely composed of metamorphic silicates. One type of contact rock consists principally of epidote, zoisite, calcite, and garnet, with a little feldspar. Another type contains calcite and zoisite in some bands and actinolite, zoisite, calcite, an undetermined isotropic mineral, and orthoclase in other bands. Pyrite is common throughout the rock.

The strikes of the limestone and of the contact are in general northwest and both dip northeast. The intrusive body is not entirely concordant however, and some limestone beds are cut out (Fig. 4).

Pyrite deposits in the vicinity are of 2 types: those in quartz veins and those in contact-metamorphosed limestone. Most of the quartz veins are in the monzonite but a few lie in limestone near the contact. One vein runs along the contact about 130 feet east of the prospect tunnel. The veins range from a small fraction of an inch up to 11 feet wide and two were traced horizontally for about 100 feet. Many of the veins strike about N. 10° west and all those observed dip east at angles ranging from 22° to 71°. The vein walls typically grade into altered and sulphide-impregnated monzonite. The vein matter is principally quartz, calcite is locally abundant, and pyrite, abundant in places, is the only sulphide recognized.

The precious metal content of most of the veins is not satisfactorily known. A sample cut across the vein that follows the limestone contact about 130 feet east of the tunnel, at a place where it is 2½ feet wide, yielded a trace of both gold and silver. The values in the vein on which the tunnel is driven are better known but even these are unsatisfactory because the samples are reported to have been cut all the way across the tunnel without separating vein matter from altered wall rock. A sample cut during this survey across a width of 6½ feet at a place about 15 feet in from the tunnel portal contained traces of gold and silver. The following table of assay results is compiled from information furnished by Wm. L. Paul, one of the owners.

TABLE SHOWING GOLD AND SILVER CONTENT OF SAMPLES CUT IN TUNNEL OF GLACIER BAY MINING COMPANY

Feet, from portal.	Back sample.		Face sample.		Floor sample		Assayer
	Au.	Ag.	Au.	Ag.	Au.	Ag.	
38	.02	—	.01	—	.02	—	Alaska Juneau Gold Min. Co.
44	.01	—	.01	—	tr.	—	" " " " "
54	.01	—	.02	—	.02	—	" " " " "
58	tr.	—	tr.	—	.05	—	" " " " "
62	.03	—	.06	—	.09	—	" " " " "
70	.01	—	tr.	—	.02	—	" " " " "
75					.05	.60	Wm. T. Burns, U. S. Geol. Survey
80	.10	.70	.03	tr.	.02	tr.	" " " " " " "
85	.10	.40	.03	.10	.25	.30	" " " " " " "
90	.14	.20	.05	.10	.10	.10	" " " " " " "
93	.04	.30	.12	.10	.08	.30	" " " " " " "
98	.51	2.4	.28	1.0	.38	.40	" " " " " " "
103	.48	1.6	.66	2.4	.32	.40	" " " " " " "

A copy of a Tacoma Smelter return on about 4 tons of selected ore reported to have come from near the portal of the tunnel shows .37 ozs. gold and .15 ozs. silver per ton.

The large ore-bearing zone along the contact northwest of the tunnel is exposed for about 250 feet. To the east it passes into a quartz vein in monzonite; on the west it is covered by talus near sea level. The zone is mineralized across a thickness of at least 10 feet and it stands nearly vertical. Mineralization consists of pyrite distributed through the contact rock and of occasional kidneys, from several inches to several feet long, of pyrite and quartz. A sample of richly pyritiferous material yielded only traces of gold and silver. The pyrite carries a small amount of chalcopyrite in tiny rounded blebs.

A similar zone crops out about 130 feet northeast of the one just described. The strikes of the two zones are about parallel but the northern one, instead of being nearly vertical, dips northeast at about 30 degrees. The rock of this zone, which here appears to be developed along a certain bed, is almost identical with the metamorphic rock along the contact and the sulphide bodies in it are also similar.

North Marble and South Marble Islands (6).

North Marble and South Marble Islands lie in Glacier Bay about half way between Sandy Cove (5) and Willoughby Island (8). According to Buddington [7] a nickel claim was staked on North Marble Island by S. H. Vevelstad.

Both Islands are constituted principally of coarsely crystalline white and blue-gray marble. The marble is cut in several directions by dark colored, fine grained, porphyritic dikes. The largest dike seen is on South Marble Island. It is about 30 feet thick.

On North Marble Island were found bodies of sulphides up to 1½ feet thick and 15 feet long. These are distributed in the marble in the vicinity of the dikes. Deposits along contacts between dikes and marble are common, and many joints in the dikes contain sulphides. The sulphides that were recognized include pyrite, pyrrhotite, chalcopyrite and covellite. Others may be present. Calcite is a common constituent of many of the deposits. Any nickel present is probably in pentlandite but that mineral was not recognized although its presence is suspected.

The sulphide mineralization on South Marble Island is similar to that on North Marble Island but does not appear to be as intense.

Francis Island (7).

An attempt to find a reported ore deposit on Francis Island was unsuccessful as the place where the deposit is reported to lie is covered with a recent landslide. The following is quoted from Buddington's notes [8]:

> Two claims (Dixon No. 1 and 2) have been staked on Francis Island, in Glacier Bay, by M. V. Manville and T. P. Smith. These claims lie along a dike of diorite which cuts across the island from the southwest to the north end. The island is composed of marble. At the southwest end the dike is about 50 yards wide and is bordered by 5 feet or so of green contact garnet rock. A few lenses of serpentine and veins of tremolite occur in the adjacent marble. Near the southwest end of the dike, on the west side, at the top of a cliff, a small pocket of bornite yielding gold and silver assays was found in the contact garnet rock. The dike at the north end is impregnated with pyrite and pyrrhotite.

[7] Buddington, A. F.: *Op. cit.*

[8] Buddington, A. F.: *Op. cit.*

Willoughby Island (8).

Two mineral deposits were seen on Willoughby Island, one in the northeast part of the island and the other about 2 miles S. of the northwest point of the island close to the southwest shore.

The first deposit is at an altitude of about 750 feet. The country rock is limestone and the ore deposit is apparently a replacement body in the limestone (Fig. 5). No intrusive rock was

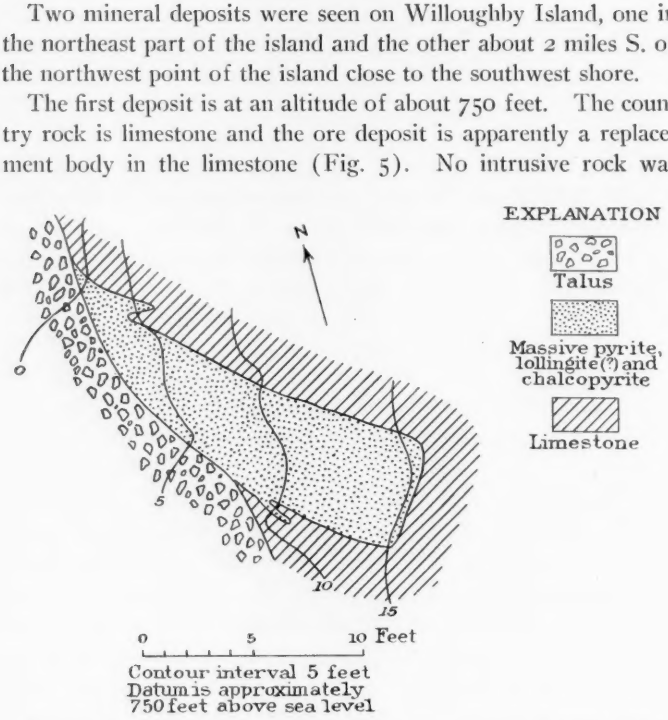

FIG. 5. Sketch of mineral deposit in northeast part of Willoughby Island.

seen in this part of the island but the place is covered with dense vegetation growing on deep forest litter and only a little rock was seen.

The deposit is exposed over an area about 15 feet long and 5 feet wide and for a height of about 15 feet (Fig. 5). One end terminates abruptly against limestone but the other end is covered with talus. The deposit is composed almost entirely of massive metallic minerals among which were recognized pyrite, an arsenic-

bearing mineral that may be lollingite, and subordinate chalcopyrite. The gold and silver content of the deposit is not known.

According to John Johnson, a fox rancher on Willoughby Island, at least 3 other similar deposits are known on the island. Johnson describes an open cut which must be near the deposit found but a search for it was unsuccessful. The cut is said to be in massive sulphides and to be about 30 feet long and 5 feet wide. In a small valley in the same vicinity Lester Rink is said to have prospected a 3-foot zone of massive sulphides.

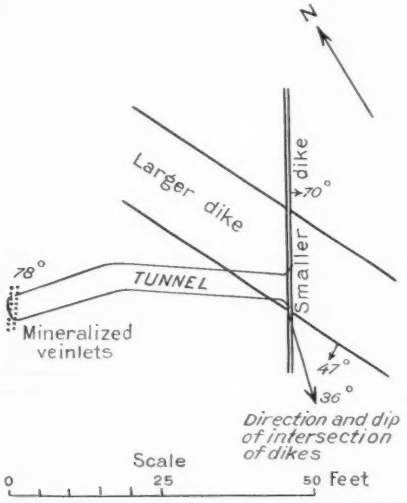

FIG. 6. Geologic sketch of prospect on Willoughby Island.

On the southwest side of Willoughby Island a little prospecting has been carried on. The prospect lies about 1¼ miles south of the northwest point of the island and about 450 feet above the beach. When visited in 1936 the prospect was not being worked and ladders and cables used to reach it were in disrepair.

The country rock is marble. The marble in the vicinity is cut by lamprophyre dikes, two of which intersect at the prospect (Fig. 6).

A thin section of one of the dikes is made up principally of lath-shaped crystals of andesine with considerable chlorite, quartz, pyroxene, and magnetite, and with a little calcite. The larger dike is 9 feet thick and trends N. 25° W. It dips 48° S.W. The smaller is 1 foot thick, strikes N. 31° E., and dips 70° S.E.

A kidney of rich ore is said to have been mined from the intersection of the two dikes at the surface. A tunnel about 50 feet long has been driven westward from that place but it apparently encountered little ore. Sulphides were observed in joints in the marble and along both contacts of both dikes, for a considerable distance away from the intersection. Clearly the mineralization is related to the dikes. Prospecting toward the S.W. and downward along the intersection of the 2 dikes might be justified.

Chalcopyrite, pyrite, and tetrahedrite are readily recognizable in the sulphide kidneys along the dikes. Another metallic mineral has not yet been identified. Buddington[9] records 25% lead, 25% antimony, 1.74 ozs. gold, and 42 ozs. silver per ton, in ore from this place. It is not clear whether this was reported to Buddington or was the metal content of samples actually collected by him. He also reports jamesonite from the northwest side of Willoughby Island, probably from the same place.

West Side of Glacier Bay South of Berg Bay (9).

Several claims were staked many years ago at an altitude of about 1,200 feet on a mountain, locally called Observation Mountain, on the west side of Glacier Bay south of Berg Bay and about half way between Berg Bay and Pt. Carolus. This place is about 1 mile from the shore but about 2 miles by an old, overgrown trail. The claims, which are reported to be now abandoned, constitute the Alaska Chief property.

The principal country rocks are marble and a contact rock consisting mostly of zoisite and epidote, with some chlorite and calcite, and a few thin veinlets of quartz and calcite. The marble contains considerable quantities of chlorite, orthoclase, and quartz. A little quartz monzonite was seen and the presence of a large body of intrusive rock in the vicinity is pointed out by the

[9] Buddington, A. F.: *Op. cit.*

Wrights[10] who visited the claims in 1906 and who say "The workings are . . . at the contact of a large diorite mass intrusive into calcareous argillites and cherts." The marble and contact rocks are locally thin bedded. The general strike is about N. 75° W. and the dip is 30° S.

Mineralization consists of replacement of marble and contact rock by sulphides. The calcareous beds appear to be more completely replaced than the epidote-zoisite rock. Replacement is widespread, intense, and locally nearly complete over a stripped area about 200 feet by 75 feet (Fig. 7). Less intense replacement by sulphides appears to extend over a much wider area.

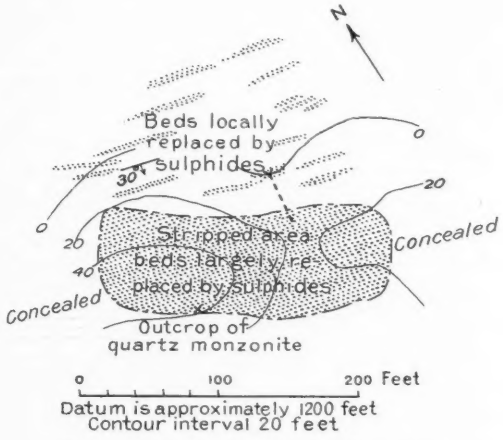

FIG. 7. Sketch of Alaska Chief prospect.

In the stripped area the sulphides are partly oxidized to limonite and copper carbonates are common. A tunnel, 40 feet long, below the stripped area encounters unoxidized sulphides. A tunnel 130 feet long mentioned by the Wrights was not found in 1936. Sulphides that were recognized include pyrite, chalcopyrite, and pyrrhotite.

[10] Wright, F. E., and C. W.: *Op. cit.*, p. 221.

Lemesurier Island (10).

Two claims have been patented by G. H. Whitney on the southern tip of Lemesurier Island about 1 mile S.W. of J. P. Ibach's house on the shore of Willoughby Cove. The claims have been long abandoned. Old development consists of a short tunnel reported to have been driven about 1916.

The prospect is at the contact of a body of quartz diorite on the west and marble on the east. The quartz diorite is made up principally of oligoclase, quartz, and hornblende. A little orthoclase is present. Epidote and chlorite are common, and apatite and titanite are present as accessories.

The contact between the intrusive rock and the marble is exposed for a few hundred feet horizontally and about 150 feet vertically. It trends about N. 10° E. The marble appears to strike about parallel to the contact and to dip toward the east.

Between the quartz diorite and the marble is a contact zone that, where observed, ranges between 20 feet and 50 feet thick. The contact rock is hornfels that is made up of pyroxene, garnet, and quartz. Some calcite is present and locally large, well-shaped apatite crystals with pleochroic cores. Opaque minerals recognized in the hornfels are molybdenite, chalcopyrite, and graphite.

The molybdenite is commonly associated with the quartz and is found disseminated through the hornfels and locally concentrated in streaks.

Buddington[11] who examined the tunnel at the prospect says, "The tunnel starts at a point on the contact between the limestone and the garnet rock. The last 25 feet of the tunnel is in banded hornstone and quartzitic beds. At the breast of the crosscut diorite is exposed. Several pockets of garnet rock are exposed along the walls of the tunnel, but the best exposures are at the surface. Molybdenite occurs as facings along small gash fractures in the contact rock and to a lesser extent in disseminated form. In most of the rock the molybdenite is sparse but small pockets are found in which molybdenite forms several percent of the rock."

[11] Buddington, A. F.: *Op. cit.*, 1924.

Chichagof Island, between Pt. Lucan and Column Pt. (11).

Five claims, comprising the Lincoln group, have been staked on the northwestward-facing mountain slope between Pt. Lucan and Column Pt. Two of the claims are owned by M. J. Marvitz, 2 by Gardner Sullivan, and 1 by J. P. Ibach. The claims are reported to have been staked first in 1926 by Marvitz. They were abandoned in 1928 and restaked in 1932.

Development consists of 3 small tunnels, the lowest and shortest one at an altitude of 850 feet, the intermediate one, which is about 50 feet long at 980 feet, and the upper tunnel, about 210 feet long, at 1,080 feet.

The country rock from the coast to the claims and apparently beyond them higher on the mountain is schist and slate. A typical specimen is quartz-sericite schist which is largely quartz and sericite but which contains also a little biotite and plagioclase.

The rocks strike between N. 25° W. and N. 35° W. and dip from 55° to 70° N.E. In addition to their planar foliation the rocks display a distinct linear foliation, or stretching, that lies in the planar foliation and dips from 0° to 15° S.E. The rocks are cut every few feet by persistent cross joints that strike between N. 47° E. and N. 50° E. and dip between 73° and 80° N.W. The cross joints therefore bear an approximately right-angle relaship to the stretching.

Quartz veins and dikes of quartz andesite on the Lincoln group of claims occupy cross joints. Several dikes up to about 4 feet thick were observed. They were fine grained, greenish-gray, unfoliated, and porphyritic. They are largely composed of sodic andesine, chlorite, and quartz. An undetermined rock that may be part of a dike crops out at an altitude of about 1,500 feet. The rock is impregnated with pyrite and a mineral resembling arsenopyrite and is reported to carry good values. This kind of rock appears to comprise a band about 20 feet thick that dips steeply and strikes about E.

The tunnels and prospect pits expose several veins, of which the widest is about 5 feet. The veins appear to be lenticular but none are exposed for a long enough distance to furnish reliable

data for generalization. Two types of quartz are recognized by Marvitz: An early barren white quartz and a late, mineralized, glassy quartz. Free gold, pyrite, and galena were observed in some of the more heavily mineralized vein quartz.

A sample cut across a vein 2 feet thick above the upper tunnel yielded a trace of both gold and silver. Another sample from a vein 3 feet thick which outcrops at an altitude of about 850 feet indicated a gold content of 0.10 ounces per ton and a trace of silver. Marvitz reports the recovery of about ½ ounce of gold from 1 wheelbarrow full of picked ore from the intermediate tunnel. A polished section of ore from a vein on one of the claims of the Lincoln group contains grains of free gold, arsenopyrite, and pyrite. These minerals are all largely confined to dark glassy quartz in the predominant white quartz.

Chichagof Island, South Side of Lisianski Inlet (12)

The property of the Apex-El Nido Mining Co., is on the south side of Lisianski Inlet and includes about 26 unpatented claims.

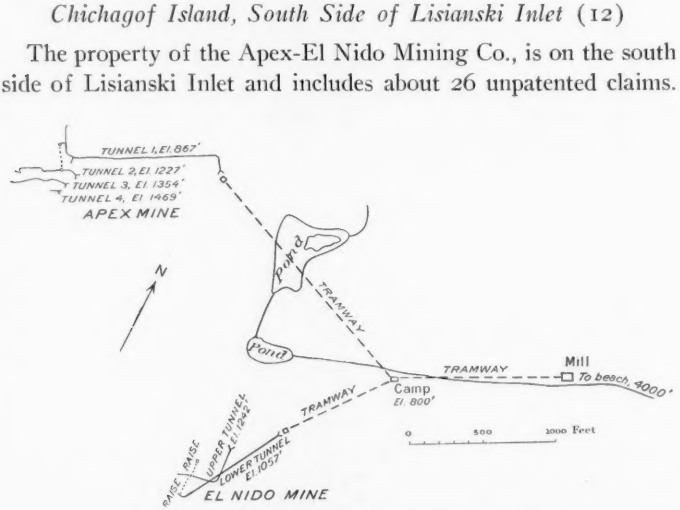

FIG. 8. Sketch of Apex and El Nido mines.

The company is controlled by Jenny R. Cann of Seattle. The principal underground development has been in two mines, the Apex and the El Nido (Fig. 8). The former is developed on 4

levels and consists of about 2,400 feet of tunnels and 1,200 feet of raises. The latter is opened on 2 levels and aggregates about 1,500 feet of tunnels and 300 feet of raises. A considerable amount of stoping has been done in the Apex mine and the ore removed is reported to have yielded about $230,000. Three small stopes in the El Nido mine are said to have produced about $10,000. Surface equipment consists of a water power plant, crusher, stamps, amalgamators, and concentrating tables, pipe lines, aerial tramways, camp buildings, and a road to the beach.

According to local reports the Apex vein was discovered in 1919 and the El Nido vein in 1920 by Jack Cann and associates. From 1920 to 1928 the property was worked by the Chichagof Mining Co. From July 1928 to 1931 the mines were not worked. In 1931 the property was optioned and some work was done by the Condor Mining Company. This company gave up its option in the fall of 1931. In 1934 and 1935 the mines were worked by a few men. Since August, 1935, the property has been shut down.

GEOLOGY.

The principal country rock in the vicinity of the Apex and El Nido mines is hornblende diorite. A thin section of one specimen is composed largely of hornblende and labradorite-bytownite. Zoisite, chlorite, pyrite or pyrrhotite, and sericite were noted also. Another section is similar except that the feldspar is andesine and a little calcite is present. Altered parts of the diorite are in places made up largely of calcite and chlorite, with remnants of plagioclase and with some leucoxene and pyrrhotite. A specimen of rock from the El Nido mine, that was thought to be part of a dike in the field, is principally crushed quartz with calcite, sericite, and pyrite. The rock is cut by many small quartz veinlets. This rock may be silicified diorite.

The Apex vein strikes about N. 60° E., and dips about 45° N.W. The vein ranges from about 5 inches to about 48 inches thick. In places the vein splits into a stockwork of branching veinlets that run in all directions. In addition to the main vein

are some small veinlets, a few inches thick, that strike about parallel to the Apex vein and which are vertical.

The El Nido vein strikes between N. 60° E., and N. 85° E., and its general dip is about 60° S.E. Its thickness ranges from about 4 inches to about 60 inches and may average about 10 inches. The vein is banded and appears more regular and more continuous than the Apex although at most places it is not as thick.

Native gold, pyrite, arsenopyrite, and scheelite were noted, in addition to quartz in vein material from the Apex and the El Nido veins. One specimen of picked ore from the Apex mine shows numerous small grains of gold in cracks in large crystals of pyrite. Another contains abundant arsenopyrite in veinlets that traverse the quartz vein parallel to its walls. A polished section of ore from the El Nido vein contains a grain of free gold and a large amount of arsenopyrite in cracks in the quartz. Assay maps of both veins indicate that the values are widely different at different places but may average about an ounce of gold to the ton.

Buddington and Chapin [12] have noted the scheelite at the El Nido mine as follows: "At the Apex-El Nido property the scheelite occurs in disseminated form in high-grade gold quartz veins associated with arsenopyrite and also in a shoot of solid scheelite 5 inches wide in a quartz stringer."

SUMMARY AND CONCLUSIONS.

It has already been pointed out that most of the deposits examined appear to be genetically related to bodies of granitic rock that were intruded probably in Upper Jurassic or Lower Cretaceous time. Exceptional deposits appear to be directly related to lamprophyre dikes which are younger than the granitic rocks. These exceptional deposits include the following: The small kidneys of chalcopyrite and pyrrhotite in calcite, and the silicious contact rocks that contain pyrrhotite, pyrite, and arsenopyrite

[12] Buddington, A. F., and Chapin, Theodore: Geology and mineral deposits of southeastern Alaska. U. S. Geol. Survey. Bull. 800, p. 330, 1929.

along dikes east of Reid Glacier (4); the bodies of mixed pyrite, pyrrhotite, chalcopyrite, and covellite on the Marble Islands (6); possibly the pyrite-lollingite (?)-chalcopyrite masses in the northern part of Willoughby Island (8) although no lamprophyre dike was found there; and the chalcopyrite-pyrite-tetrahedrite-jamesonite (?) deposit on the southwest side of Willoughby Island (8).

The relationship between the granitic rocks and the ore deposits in southeastern Alaska has long been recognized. Buddington and Chapin[13] go further to say: "Accepting this generalization concerning origin as valid, we face the question whether a particular type of mineralization is prevalently associated with a particular type of mode of occurrence of igneous rock; or with a particular type or stage of differentiation of the magma; or with a particular type of country rock that has certain specific characters, chemical or physical, or both; or with a particular environment of temperature and pressure; or whether it is dependent upon two or more of these factors to varying degrees."

The degrees to which these factors were important in the formation of the mineral deposits of Glacier Bay and vicinity are not yet known and will not be known until much more detailed geological work is done.

Most of the deposits examined appear to belong to types formed at intermediate temperatures at considerable depths below the earth's surface. Some, for example, the contact molybdenum deposit on Lemesurier Island (10), were probably formed at high temperatures.

The deposits examined include both fissure veins and deposits formed by replacement at or near contacts of granitic masses. Some fissure veins are in the granitic rock as at Reid Glacier (4), others are in older sediments as on Chichagof Island between Pt. Lucan and Column Pt. (11).

One of the most outstanding features of the deposits is the unusual diversity of metals present in different deposits that are

[13] Buddington, A. F., and Chapin, Theodore: Geology and mineral deposits of southeastern Alaska. U. S. Geol. Surv. Bull. 800, p. 374, 1929.

not widely separated. The metals represented include iron, copper, nickel, gold, silver, lead, zinc, tungsten, and molybdenum. Why similar intrusive rocks should develop such diverse types as pyritic contact deposits with a little chalcopyrite at some places, such as Sandy Cove (5) and along the north shore of Reid Inlet (3) and contact deposits characterized by pyroxene, garnet, and molybdenite at other places such as on Lemesurier Island (10) is not known.

U. S. Geological Survey,
Washington, D. C.,
July 1, 1937.

EDITORIAL

THE AERIAL, GEOLOGICAL, AND GEOPHYSICAL, SURVEY OF NORTHERN AUSTRALIA

A brief note on recent and current official action taken to advance the development of a large region in tropical Australia, through the Mining Industry, may be of interest to readers of ECONOMIC GEOLOGY.

As an introduction to the subject, it is noteworthy that the discovery of gold, in payable quantities, in 1851, first drew the attention of the outside world, generally, to the real commercial importance of Australia. Prior to that date the value of its expectation, as an important centre of settlement, had been almost negligible.

In the decades preceding the discovery of gold, Australia just "grew." At the outset it was a British penal station, and ordinary settlement caught on where it could. There was little that was spectacular in that growth beyond the courage and pertinacity of the early explorers and the "settlers" in holding on, in the teeth, as it were, of "armed antagonisms." The pioneers found Australia a "barren" wilderness, which, in this feral stage, seemed incapable of supporting, unaided, even small civilized communities. This, in great measure, was an expression of its peculiar geological structure, whereby it had become isolated, for a lengthy period, from the great world centres of organic competition. This "Safety First" measure was not an unmixed blessing; it protected the Australian organisms from severe external interference, but it was inimical to keeping abreast of world progress; it allowed the law of "Age and Area" to operate harshly against Australian advance. Naturalists stigmatized it as "the home of lost causes." Relics of ancient life such as the

" Port Jackson shark," the " Queensland mudfish," the egg-laying (monotremes) and the pouch-bearing (marsupials) mammals, together with a host of other relatively inefficient associates, had been gathered into Australia as into a sanctuary, an ancient " City of Refuge." The drawbridge which once connected Australia with the great northern lands had disappeared, and organisms in the " sanctuary " had stagnated, while plants, such as support vast civilizations in the northern hemisphere, and animals which followed on the heels of such excellent food, were developed in that great outer world.

Then, with dramatic suddenness, came the irruption of the British with their official institutions, together with their demand for the ordinary amenities of civilized life. Visitors to the island continent to-day find themselves unable adequately to conceive the backward state of Australia one hundred and fifty years ago. But the occidental spirit of unrest, and desire to succeed, were inborn in the pioneers of civilization in this southern outpost. Subsisting mainly, at the outset, on outside supplies, they straightway faced the severe problems of geographical exploration in this great lone land, in the hope of ascertaining to what extent it might be made self-supporting. It had 3,000,000 square miles of territory, an area equal to that of the United States. But the grains, vegetables, fruit, and live stock imported needed adjustment to the strange Australian conditions. Years passed in agricultural experiments. Other serious problems confronted the " colonists "; metallic materials, in commercial quantities, had not been found. Ever with these colonists were the nightmare of insecurity, the dread appreciation of the saying " Woe to the nation " which may have agricultural wealth, but no adequate mineral supplies to protect them, a land where one may sow and another reap.

In this general discouragement came the discovery of gold, in payable quantities, in 1851, by Hargreaves, an Australian pioneer, who knew California during its early gold mining days, and who had called to mind the existence of similar " placer " deposits (" leads ") in his homeland of New South Wales. With the opening up of these gold " placers," and of the associated vein

deposits, the advancement of Australia was assured straightway. Adventurous spirits poured into Australia from all quarters of the globe. The halo of romance was now upon the once-despised land. Discoveries of gold deposits followed each other in rapid succession as prospecting operations were extended afield. Valuable discoveries of mineral deposits other than gold were made also during the feverish search for gold. Settlement followed closely on the heels of individual "finds." Ballarat and Bendigo in Victoria; Mount Lyell and Mount Bischoff in Tasmania; Iron Knob, Iron Monarch, with Wallaroo and Moonta, in South Australia; Mount Morgan and Mount Isa in Queensland; Broken Hill, Cobar, and the New England tin districts, in New South Wales, may be mentioned as illustrations.

The total value (pre-War standard) of gold won from the Australian fields, to date, is, approximately £700,000,000, while that of all minerals won is about £1,400,000,000.

Following on this prosperity, the decline, in recent years, of the gold-mining industry in Australia, was regarded, both officially and generally, with grave concern. That same industry had shown that Australia was not, necessarily, the home of lost causes only: Nature, in the dim geological past, had not been unmindful altogether of its isolated offspring, Australia. Certain mining authorities at this stage considered that an application of modern scientific methods might revive the languishing industry. Sir Herbert Gepp, Director of the Federal Development and Migration Commission, voiced this growing opinion. Australian wheats and wool had won golden opinions from the outside world by the application of scientific methods to their development. Was it not possible, also, that the Mining Industry of which he had once been a prominent member (General Manager of the Electrolytic Zinc Company, Australasia) might rise again to a position of great importance, if approached with a full knowledge of modern geological and geophysical methods?

As a beginning, the formation of a Federal Geological Survey was advocated strongly. This project has been deferred, assurance being sought by some States that a Federal Survey should

be formed in a manner such as to be of definite assistance to Australian geology as a whole. The New South Wales Government, however, had already attached a young geophysicist to its Geological Survey.

In the meantime it was well known to mining geologists that the great positive "nuclei" of Australia were composed of "archæan" rocks, and that these "nuclei" comprised the greater portion of the Northern Territory, Western Australia, and northern Queensland, together with large areas in South Australia and New South Wales; moreover, that these areas had yielded very valuable mineral deposits, such as Kalgoorlie, Broken Hill, and Mount Isa. These vast tracts of country too often have been considered as waste lands, inasmuch as they present almost insuperable difficulties to the individual prospector, possessed only of very slender resources; their surfaces lack marked vertical relief, being flat or undulating; the solid rock masses of which they are built are concealed, in great measure, beneath a cover of subhorizontal and "non-mineralized" deposits of late pre-Cambrian, early Palæozoic, Mesozoic, and Cainozoic, sediments; they support a sparse and xerophytic vegetation; their surfaces, in the more arid portions, are desolated by wandering sand-ridges and by blinding "sand-storms," born of the winds that frequently rage through the interior; they lack water supplies, except at the all-too-infrequent wells and "soaks"; and in a long drought water supplies, in many places, may fail altogether.

While the writer was in Ottawa, in 1927, he learned from the Director of the Canadian Geological Survey (the late W. H. Collins) of the formation of an "Imperial Geophysical Survey," proposed for application to Australian conditions, the Director having been selected, and, moreover, the scope of the time limit of, and amount of money to be expended on, the Survey having been practically decided. At a later stage, the State Governments co-operated with the Survey in an advisory capacity.

This Imperial Survey was conducted in Australia for a period of three years, and a report of its main activities was published. The electromagnetic section of the work, which had been en-

trusted to Dr. Bieler, of McGill University, was, upon his lamented death, entrusted to, and written up, by J. M. Rayner, the geophysicist to the Geological Survey of New South Wales.

This stage completed, another phase was entered, and the accompanying note is a summary statement of a more recent official undertaking.

The results gained both by the work of the Imperial Geophysical Survey and that of representatives of recognised private geophysical groups appeared promising, and an official Survey was formed to assist prospecting work in Northern Australia.

The genesis of the Survey was developed in conferences between the Commonwealth, Queensland, and Western Australian, Governments, in which it was decided to make a " geological and geophysical reconnaissance of the mineral-bearing regions of Northern Australia, in order to advance the development of this part of the Commonwealth through its mining industry."

The Commonwealth Government undertook to provide a sum, having its upper limit at £75,000, the two State Governments concerned deciding each to provide £37,500, on a basis of three years' work. The Survey is controlled by a Ministerial Committee consisting of the Hon. A. J. McLachlan, Federal Minister in charge of developments, the Hon. T. A. Foley, Minister for Mines, Queensland, and the Hon. S. W. Munsie, Minister for Mines, Western Australia. It is a matter of intense satisfaction that the interest taken by the Ministerial Committee promises to give an extension of two years to the Survey on the same scale as during 1937. The official heads of the two State Geological Surveys (L. C. Ball, Queensland, and F. G. Forman, Western Australia) were appointed members of the Executive Committee, with P. B. Nye, State Geologist of Tasmania, as Executive Officer, and Sir Herbert Gepp as Director of the Survey. W. G. Woolnough, the Commonwealth Geological Adviser, was appointed Geological Consultant to the Executive Committee, and J. M. Rayner, with the consent of the New South Wales Government, was appointed " Consultant Geophysicist to the Survey." Equipment for the electrical methods of prospecting was obtained from

the "Electric Prospecting Company of Sweden" under the direction of S. Howarth until the close of the year 1936. Since that date the Survey has designed and controlled most of its equipment.

The Survey was confined to the search for metallic minerals, particularly gold. Three geophysical parties have been appointed, each party containing three geophysicists, ample assistance being provided for camp and transport facilities.

The scope of the Survey included aerial, geological, and geophysical surveys, with provision for boring and other methods of testing the findings of the survey parties. The title of the undertaking is "The Aerial, Geological, and Geophysical Survey of Northern Australia."

The Survey was commenced about the middle of 1935, and the expenditure on its activities until the end of 1936 has been £75,000 approximately.

Two years' work appears to justify the Survey in directing the attention of mining interests to various areas in Northern Australia. Among these areas of apparent promise are:

(1) The Kimberley and Pilbara districts in Western Australia.

(2) The Claudie River Gold Field (in the northern part of Cape York Peninsula), the Croydon Gold Field, the Hodgkinson, Etheridge, and Cloncurry, districts, in north Queensland.

(3) The Pine Creek district, Tennant Creek Gold Field, Daly River District, and the eastern Macdonnell Range, in the Northern Territory.

Most of these areas are gold fields. The Tennant Creek and Claudie River Fields are selected for brief separate description in this *Journal*, as illustrating the general geological conditions in certain mining areas in Australia, which are but little known to the geological world. In these two areas very promising results have been obtained by the geophysical parties.

For more detailed accounts of the Survey and its activities, reference may be made to the voluminous reports by the Commonwealth Government (Canberra, F. T.) on the "Aerial . . . Survey of Northern Australia," for the period 1934–1937.

E. C. ANDREWS.

DISCUSSION AND COMMUNICATIONS

EFFECT OF A SEA-LEVEL CANAL ON THE GROUND-WATER LEVEL OF FLORIDA.[1]

Sir:—The paper by Sidney Paige entitled "Effect of a sea-level canal on the ground-water level of Florida," in the September-October, 1936, issue of Economic Geology, deals with a subject of much scientific and economic interest about which wide differences of opinion have been expressed. The writers of this discussion have long been serious students of ground water problems including those of Florida. They find much of interest in Mr. Paige's paper and much with which, to their regret, they are unable to agree. In the interest of sound scientific progress it is believed to be worth while to present here certain points of view which it is hoped may help to clarify the problem.

PERMEABILITY OF THE OCALA LIMESTONE.

The principal water-bearing formation that will be cut by the canal, if one is constructed, is the Ocala limestone, and one of the major ground-water problems involved relates to the permeability of this limestone at considerable depths. The Ocala limestone is not definitely described in Paige's paper, and the reader must depend, for his knowledge of it, on brief statements scattered here and there through the text. Paige states that it has "considerable porosity" (p. 558) and that flow is taking place through the porous rock at all fresh-water depths (p. 557). He recognizes the presence of numerous water-bearing solution cavities (pp. 543–545) and refers to "the development of cavities and solution passages within that portion of the Ocala limestone that stands today or has stood in the past for long intervals above the

[1] Published by permission of the Director, United States Geological Survey.

level of the water table" (p. 558). He considers, however, that the process of the formation of solution cavities is largely a "superficial" phenomenon (p. 545), and he bases his conclusion as to the effects of the canal in part on the assumption that it "will traverse an area wherein resistance to flow of water through the rocks will be substantially higher than in areas wherein underground drainage gradients have been during a long period reduced to graded slopes" (p. 568). The plan for safeguarding Silver Springs and Blue Springs noted by him (p. 569) is also evidently based on the assumption, for which he presents no specific evidence, that the permeability of the Ocala limestone is largely a superficial phenomenon.

It has long been recognized by geologists that an outstanding feature of the limestone in Florida is its great permeability to depths of at least several hundred feet. This condition has been explained in part by the loosely coherent, granular character of much of the rock, and in part as the result of the former greater elevation of the land in relation to the sea, and the consequent lowering of the water table, and development of extensive solution openings at considerable depths.[2] It is clear that this latter condition accords in general with the now accepted theory of lowering of sea level during the glacial stages of the Pleistocene.

A report of the U. S. Army Engineers[3] shows the logs of test borings along the proposed route of the canal. In the 45-mile stretch between the longitude of Silver Springs and the Gulf of Mexico, the route is essentially in the area of outcrop of the Ocala limestone except that the surface material is described as sand and clay. In this stretch 61 borings penetrated the Ocala limestone to a depth of 10 feet or more. Nine of these encountered cavities below the water table, and in 8 others sand or clay was found interbedded with the limestone in a manner to suggest pockets filling solution cavities. Many of the borings did not go deeper

[2] Meinzer, O. E.: The occurrence of ground water in the United States, with a discussion of principles. U. S. Geol. Surv. Water-Supply Paper 489, p. 132, 1923.

[3] Waterway from Cumberland Sound, Georgia and Florida, to the Mississippi River. Rept. of Special Board, Appendix B, Geology and Ground Water, Dec. 30, 1933.

than 20 feet below sea level, as the exploration was apparently for a lock canal, as originally planned. Only a few borings went deeper than 50 feet, but several entered cavities between 25 and 50 feet below sea level. In the only core boring carried to a depth of 100 feet below sea level (no. 17–A), a cavity was found about 75 feet below sea level. About 12 miles out in the Gulf of Mexico, where the water is about 25 feet deep (core boring no. G–12–1/2) a cavity was found about 14 feet below the top of the Ocala limestone and about 42 feet below sea level; and in a boring on the floor of the Gulf about a mile nearer the shore, a cavity was revealed at a depth of about 34 feet below sea level.

In addition to the borings that encountered cavities, there were 9 borings that reached the top of the Ocala at considerably lower levels than it was reached in borings a few hundred to a few thousand feet on each side; and in a cross section these were interpreted as being in "solution depressions." The presence of most of these depressions was not suggested by surface topography. Several of the depressions extend about 50 feet into the rock. One such depression (in core boring no. 19B) at the Dunellon lock site, extended to a depth of about 75 feet below the general surface of the bedrock and about 45 feet below sea level.

The borings obviously tested only a very small part of the entire 45-mile stretch of outcrop area. However, if the distribution of cavities or solution depressions in the whole stretch is in proportion to those found in the small part of it that was tested, it is evident that cavities and depressions occur at some depth below the water table along a total length of several miles.

Further significant information as to the permeability of the Ocala limestone is found in the report of the U. S. Army Engineers just mentioned, in tables showing "record of drill water losses" in test holes bored at the proposed Orange Creek, Dunellon, and Inglis lock sites. The loss is reported as 100 per cent. in the lower part of 4 out of 8 holes at the Orange Creek site; 100 per cent. in the lower part of 8 out of 9 holes at the Dunellon site; and 100 per cent. in the lower part of 3 out of 7 holes at the Inglis site.

In Orlando and vicinity much of the rain water and sewage is drained into the Ocala limestone through wells that range in depth from 160 to more than 800 feet.[4] The wells generally enter cavities with large intake capacity. One well,[5] 16 inches in diameter and 383 feet deep, is reported to have an intake capacity of 9,500 gallons a minute. The logs of many drainage wells drilled for the city of Orlando at sites ranging from about 60 to 100 feet above sea level show cavities at considerable depths, some of them as much as 600 to 700 feet below sea level. Thus, in well 12 cavities occur at depths of 162, 460, and 483 feet; in well 14 a cavity 28 feet deep extended between the depths of 349 and 377 feet; in well 17 a cavity 18 feet deep extended between the depths of 465 and 483 feet; in well 9 a 10-foot cavity was found at 455 feet, a 2-foot cavity at 775 feet, and a 2-foot cavity at 794 feet. Cavities ranging in size from 1 foot to as much as 14 feet are reported in 17 other wells at depths ranging from 175 feet to 495 feet. In 7 of these wells the cavities were at depths greater than 400 feet, and in 5 wells they were at depths between 300 and 400 feet. Cavities were reported in all except 2 out of 23 city wells for which fairly adequate logs are available. According to information available, well 2 of the Oil Development Co. of Florida, in T. 24 S., R. 25 E., in Lake County, is 5,500 feet deep and struck a small cavity at a depth of 120 feet, a 6-foot cavity at a depth of 299 feet, and other cavities at depths down to 1,880 feet.

The public water supply of Jacksonville is obtained from wells 700 to 1,000 feet deep, drawing from the Ocala limestone, which here lies beneath about 500 feet of the Hawthorn formation.[6] The record of city well 10 shows that at a depth of 270 feet, in the Hawthorn, the yield, by natural flow, was only 5 gallons a minute; at a depth of 900 feet, in the Ocala limestone it was 900

[4] Stringfield, V. T.: Ground-water investigations in Florida. Florida Geol. Surv. Bull. 11, pp. 17–24, 1933.

[5] Orange County well 16, Stringfield's Orange County no. 50, Water-Supply Paper 773–C, pp. 161 and 185, 1936.

[6] Stringfield, V. T.: Ground-water investigations in Florida. Florida Geol. Surv. Bull. 11, p. 28, 1933.

gallons a minute, and at a depth of 980 feet it was 1,500 to 2,000 gallons a minute.[7]

In 1886–87 a well 12 inches in diameter was drilled to a depth of 1,390 feet at the Ponce de Leon Hotel in St. Augustine.[8] It is said to have yielded, by natural flow, 3,000,000 gallons a day (about 2,100 gallons a minute) at a depth of 410 feet. At 520 feet the yield increased to 7,000,000 gallons a day, and at 1,100 feet it was 10,000,000 gallons a day (about 7,000 gallons a minute) with a head of 42 feet. This well apparently held the record for many years for having the largest yield by natural flow of any well in the world.

The American Agricultural Chemical Co. has several wells near South Pierce, in Polk County, with very large yields from the Ocala limestone. Its well 7, which is 850 feet deep, has been pumped 7,500 to 8,000 gallons a minute (approximately 11,000,000 gallons a day). It is reported that at the bottom of the well, 700 feet or more below sea level, the drill tools dropped into a cavity about 7 feet deep. The logs of the other wells show that much of the water was obtained from "cavities" or "porous rock" at depths ranging from 730 to 790 feet.

It may be added that the Ocala limestone in the southern part of the State, at a considerable distance south of the proposed canal, where the ground water will not be affected by the canal, is not so permeable as that in the area to the north. The specific capacity[9] of wells penetrating the Ocala in the southern part of the State is noticeably smaller than the specific capacity of wells penetrating the Ocala farther north. Exploration of several wells in the vicinity of Sarasota by the deep-well current meter has shown that in that vicinity less water comes from the Ocala limestone than was supposed, and that much of the water comes from the Tampa limestone and the lower part of the Hawthorn formation.[10]

[7] Sellards, E. H., and Gunter, Herman: The artesian water supply of eastern and southern Florida. Florida Geol. Surv. 5th Ann. Rept., pp. 146–147, 1913.

[8] The great artesian well at St. Augustine, Fla. Eng. News, vol. 21, pp. 300–301, 1889.

[9] Stringfield, V. T.: Artesian water in the Florida Peninsula. U. S. Geol. Surv. Water-Supply Paper 773–C, p. 159, 1936.

[10] Stringfield, V. T.: Exploration of artesian wells in Sarasota County. Florida Geol. Surv. 23d–24th Ann. Repts., pp. 195–227, 1933.

The evidence that has been cited, together with other well data and reports of drillers, indicates that in the central and northern parts of the Florida peninsula the Ocala limestone contains cavities and has free circulation of water to depths not merely a few feet below the water table, or to the depth of the canal, but to depths of several hundred feet. The hydrologic significance of this evidence is that the construction of the canal may adversely affect the head of the ground water to considerable distances. No specific data are cited in the paper by Paige to prove that the high permeability of the Ocala is confined to a shallow zone, and his conclusion that neither Silver Springs nor Blue Springs will be injured because dams " with properly designed water cut-offs will be constructed " (p. 569) is unsupported by pertinent geologic evidence to show that such dams will be effective.

Artesian Conditions.

It is unfortunate that so many confusing statements about hydrology have been brought into the literature through Paige's paper. Some of these are of minor character—for example, the author speaks of " the top of the water table " (p. 568) as if it could also have a bottom, and he speaks of " porosity " (Fig. 4, pp. 546, 551, etc.) when he means permeability, apparently ignoring the fact that a rock may have high porosity and yet be quite impermeable.

In the discussion of principles on page 545, the curious and incorrect statements are made that " with a fixed rate of lateral flow the curvature of the water surface will vary with the rate of rainfall," and that " with a fixed rainfall rate the curvature will vary with the rate of lateral flow of water through the rock." On page 546 the statement is made that " if the rainfall is sufficient to raise the surface of the ground water to the surface of the land at any place, then a surface run-off will be initiated." This statement seems to imply that there is no surface run-off unless the water table is at the surface and betrays a disregard of the limitations of intake facilities which vitiates much of the succeeding discussion. On page 557 the statement is made " in

Florida measurements indicate that between a third and a half of the rainfall on surfaces lying above the water table in the open reservoirs enters the reservoir, the remainder being lost in evaporation or transpiration of plants." In view of the definition of "the open reservoirs" on page 563, this statement implies that there is no direct run-off in Florida except where flowing wells can be obtained, a postulate which is contrary to the facts.

Paige says (p. 559) "it can be shown that the intake area of the reservoir comprises an area that embraces 44 per cent. of the peninsula," but he does not indicate how this high percentage was computed. Apparently it merely represents the part of the peninsula in which flowing wells cannot be obtained, but he has not shown that all of the nonflowing area is intake area. Much of the nonflowing area is underlain by the beds that confine the artesian water in the adjacent area of artesian flow and in a part of the nonflowing area the artesian water rises in wells above the water table.

Paige states (p. 541) that "from the standpoint of water storage the formations exposed and for a considerable depth below the surface are susceptible to an important distinction and subdivision." He groups all the formations in "an upper series" and "a lower series." The distinction between these series given on page 553 is that the upper series yields water with relative difficulty, and the lower series yields it relatively freely because channels have been developed within it. (See also p. 556.) This is obviously a matter of permeability and not of water storage. If such a division is to be made in this area, the lower part of the Hawthorn formation should be included in the "lower series" because, as stated in Water-Supply Paper 773–C, p. 130, the artesian pressure in it is comparable to that in the Tampa and Ocala limestones, indicating connection with these horizons.

The terms "open reservoir" and "closed reservoir" are used in many places before they are defined, on page 563, as follows: "The term 'open reservoir' refers to that portion of the Floridian plateau wherein water, in cased wells, either penetrating the Ocala limestone or the upper series, on which part of the rain-

fall is absorbed and percolates downward to the reservoir, will not rise above the ground surface. The term 'closed reservoir' refers to that portion wherein water will rise above the surface in cased wells penetrating the Ocala limestone or certain horizons in the upper series, through which any leakage is upward, and no water from rainfall directly enters the reservoir."

These terms appear ill-chosen because they suggest that there are two different reservoirs—an erroneous concept which the author evidently does not intend to present. The definitions leave a no-man's-land between the "open" and "closed" reservoirs, in which the water may be under artesian pressure, so that any leakage is upward, but in which the water in cased wells is not under sufficient pressure to rise above the surface. In determining the difference between an "open" and a "closed" reservoir, is the controlling factor artesian flow above the land surface, or is it percolation into or out of the formation? According to the definitions given, in a region of low artesian head with reference to the surface and at least a small amount of surface relief, each hill where wells do not flow would be underlain by an "open reservoir" and would be separated from numerous neighboring "open reservoirs" by the "closed reservoirs"—that is, by the areas beneath the valleys where the wells flow—even though in both "open" and "closed" reservoirs the piezometric surface is above the water table and no intake can occur.

The paper under discussion seems to go to the opposite extreme on page 551 and following pages, in saying that "the greater part of the State of Florida is underlain by an immense body of fresh water" which "should be regarded as a single great reservoir" and that the water in the "upper series" and in the "lower series" acts as a unit. Actually, where the "upper series" occurs the water table is generally an entirely different surface from the piezometric surface of the water in the "lower series." The water table is generally at a different height—in some places above and in others below the piezometric surface; its shape differs from that of the piezometric surface; it is more irregular; and in some places it slopes in the opposite direction. Over large areas these two bodies of ground water do not in a true sense act as a unit.

Considerable specific evidence in support of these statements can be presented, of which the following are examples: The artesian head in drainage wells close to certain lakes in and near Orlando is at times above the level of the lakes and at other times below that level. Wells tapping the Ocala limestone on the south and west shores of Lake Apopka have a head several feet above the lake, but north of the lake, the artesian head is several feet below the level of the lake. The head on the water in a well drilled into the Ocala limestone at a point only 25 feet from Lake Weir has stood from 21 inches to several feet below the level of the lake since the well was drilled in 1931; and the maximum fluctuation of the head in the well has been about four times that of the level of the lake. A somewhat similar relation has existed in a well only 20 feet from Lake Ariana at Auburndale. Observations in the Cosme-Odessa well field of the Pinellas Water Company, in Hillsborough County, show no relation between the level of several lakes and the head of water in the Tampa and Ocala limestones; and there is some evidence that the water table of the surficial beds slopes in a different direction from the piezometric surface of the water in underlying limestones.

It should be noted that the piezometric surface shown on plate 12 of Water-Supply Paper 773–C does not represent the head of the water in the Ocala limestone alone, as indicated by Fig. 8 (p. 552) of Paige's paper, but also the head of water in the Tampa limestone, where it is present, and in some localities on water in the lower part of the Hawthorn formation.[11] Stringfield's inclusion of data for certain wells drawing from the Hawthorn was justified by the observation that in such wells the pressure head in the lower part of the formation is comparable to that in the underlying Ocala and Tampa limestones,[12] a condition that is possible if there is free communication between the Ocala and Tampa and the lower part of the Hawthorn. He distinguished, however, between wells tapping these lower beds and wells that end in the upper, less permeable part of the Hawthorn. To draw

[11] Stringfield, V. T.: Artesian water in the Florida peninsula. U. S. Geol. Surv. Water-Supply Paper 773–C, p. 146, 1936.

[12] *Idem*, p. 130.

a reliable contour map of the water table where it occurs in the upper part of the Hawthorn or in younger formations, with its numerous irregularities, would require many more observation wells than were used as a basis for Stringfield's map of the piezometric surface of the lower formations.

Under artesian conditions changes in head involve the removal of only relatively small quantities of water stored in the artesian aquifer, except in or near the intake areas where a water table exists. Changes in artesian head accordingly may be transmitted rather rapidly and for long distances without producing appreciable effects on lakes or streams in localities where the aquifer is overlain by an impermeable confining bed, but such changes may produce noticeable effects on the water table and on streams or lakes in the intake area at a considerable distance. Thus, the results of change in head in the Ocala limestone following the construction of the canal may differ greatly in different localities according as artesian or water-table conditions exist.

Paige has said elsewhere that the canal will not anywhere cut the "artesian reservoir."[13] He omits this statement from the paper under discussion but nevertheless fails to consider what appears to be a serious problem connected with such cutting. Along the route of the proposed canal the Ocala limestone passes under cover of relatively impermeable beds about 3 or 4 miles south-southeast of Silver Springs. The sea-level canal would be cut to a depth of 30 or 33 feet below sea level. The cross section of the canal route as given in Fig. 10 (p. 564) shows that the Ocala limestone extends within 30 feet of sea level for a continuous stretch of about 20 miles northeast from the point where it descends steeply beneath the "upper series" near Silver Springs; beyond that it rises within 30 feet of sea level at three points, the farthest of which is nearly 35 miles along the canal route from the point where the Ocala passes under cover. In Fig. 10 the symbol of diagonal lines that presumably indicates the Ocala limestone in the west half of the cross section is shown

[13] Paige, Sidney: Effect of cross-Florida ship canal upon the underground-water reserves (abstract). American Water Works Assoc., Florida Section, Proc. 10th Ann. Meeting, p. 6, 1936.

also east of Jacksonville (miles 6 to 25), although actually in that locality the Ocala lies at a depth of several hundred feet. This discrepancy raises a question as to the accuracy and proper interpretation of the 35-mile stretch which, in Fig. 10, is labelled "Possibility of cutting Ocala limestone." Along this stretch, if Fig. 10 is correct, the Ocala would be cut where the water is under artesian pressure. Even if it is not correct, at least a large thickness of the confining beds will be removed, and there is a possibility that the artesian pressure will cause the water to break through them.

At Sharpes Ferry, on the floodplain of the Oklawaha River, 4 miles southeast of Silver Springs, the artesian head, as shown by observations on a flowing well made frequently since January 1933, has ranged from about 45 to 53.3 feet with reference to sea level.[14] To judge from the record of a well near Orange Springs which is believed to penetrate the Ocala limestone (Marion County well 29, Water-Supply Paper 773–C), the artesian head along the canal route near the mouth of Orange Creek may be nearly as great. The cutting of the artesian part of the Ocala limestone will undoubtedly cause a drop in head, which will be transmitted to considerable distances. It may be expected to reduce the head of flowing wells in parts of the St. Johns River Valley and along Lake George and to cause an increase in the chloride content of the ground water.

Whenever in the area of outcrop of the Ocala limestone the lowering of the water table will extend to the edge of the covered part of the Ocala, either south or north of the canal route, that effect may be transmitted considerably farther into the artesian part of the reservoir as a reduction in pressure head. Obviously this will happen where the edge of the confining beds is near the canal route, but there is also the question as to the extent to which the artesian head may be affected by a drop in the water table where the Ocala passes under cover at more distant points.

[14] See Marion County well 5, Water-Supply Paper 773–C, pp. 170, 182, 192; also other unpublished measurements (weekly since January 6, 1934) on file in the U. S. Geological Survey.

Effects on Ground-Water Levels South of the Canal.

In the paper under discussion Paige states that the water table will be depressed along the canal in the area of outcrop of the Ocala limestone, and he attempts to estimate the slope of the water table toward the canal and the distance from the canal in which there will be a drop in water level (pp. 565–568). His discussion is based chiefly on the map of the piezometric surface taken from the report by Stringfield.[15]

In Fig. 11*A*, Paige shows a relatively steep "hypothetical slope that has been drawn from canal level at *C* (Fig. 8) to a point about 10 to 15 miles south of the canal where this hypothetical slope meets the established gradient." Though it is not so stated we infer that "the established gradient" means the gradient under present natural conditions.

As justification for his hypothetical gradient Paige cites the steep slopes of the piezometric surface in other parts of the peninsula (Fig. 11, *B* to *G*). Some of these are far from the proposed canal, and Paige seems to ignore the principles previously recognized by him (p. 545) that the curvature of the surface of a body of ground water is determined by "(1) the rate at which the water is supplied from above; (2) the resistance offered by the rock to the lateral flow of the water through it to some outlet." He also ignores other essential factors, though he alludes to some of them at the top of page 566. In effect, he appears to have picked out the steepest gradients to be found almost anywhere on the peninsula, regardless of whether the areas in which they have been found differ from the area adjacent to the canal in supply of water, intake facilities, area of cross section, or permeability of the rocks; but from these he has assumed that there will be a comparable steep gradient after the canal has been dug.

[15] Stringfield, V. T.: Artesian water in the Florida peninsula. U. S. Geol. Surv. Water-Supply Paper 773–C, published Sept. 25, 1936. Preliminary results were published as follows: Stringfield, V. T., and Westendick, F. C.: Artesian water in the Florida Peninsula. Florida Section, Am. Water Works Assoc., Proc. 9th Ann. Convention, March 27–30, 1935. Stringfield, V. T.: The piezometric surface of artesian water in the Florida Peninsula. Am. Geophysical Union Trans., 1935, pt. 2, pp. 524–529, 1935. The complete report was made available in manuscript form to Mr. Paige and his colleagues of the U. S. Army Engineers in the fall of 1935.

In Fig. 11 the average slope in the selected areas, in feet per mile, is as follows: *B*, 3.9; *C*, 3.8; *D*, 6.0; *E*, 2.1; *F*, 12.5; *G*, 5.0. The hypothetical gradient near the canal as shown averages about 4 feet per mile. The range is considerable and does not bear out the statement (p. 566) that the hypothetical gradient is very little different from the other gradients shown in Fig. 11. These gradients are to be contrasted with the present average gradients of about 1.25 feet per mile along the stretch shown in Fig. 11 *A*, about 1.2 feet per mile along line *AC* in Fig. 8, and about 1.5 feet per mile along the line *AB* in Fig. 8.

Profiles *B* and *D* in Fig. 11 are for localities where the surface rock is Tampa limestone, which may be less permeable than the Ocala limestone in the area that would be traversed by the canal, and may therefore require a steeper gradient to produce an equal flow of water. To judge from the geologic map of Florida, profile *C* is for a locality where the land is swampy over a large area. This suggests local conditions of low permeability, with a sudden drop of the piezometric surface as it approaches the Suwannee River.

Profile *F* shows the slope of "a small isolated high just east of Dunellon." The State geologic map shows that in this locality the Ocala limestone is overlain by the Alachua formation. The logs of test holes of the U. S. Army Engineers show that either clay or a mixture of clay and sand overlies the Ocala limestone where this "high" of the piezometric surface is found. Furthermore, according to the logs of several holes bored in close proximity to test a proposed lock site on the western edge of the "high" (core borings 19 to 19–J, inclusive), the water table drops about 10 feet in a distance of 500 feet or less, undoubtedly signifying some unusual condition. The data suggest that the water table here may be perched, with a ground-water cascade to the piezometric surface of the Ocala at the edge of the intervening clay beds. At any rate there can be no warrant for citing the gradient in this locality as in any way typical for the general area to be affected by the canal.

Profile *G* is in a locality close to the dam of the Florida Power

Corporation near Inglis, where, as shown by the contours on Fig. 8, heavy southward leakage from the pool behind the dam undoubtedly occurs, and therefore this profile can not be considered to show a typical slope.

Of all the profiles of the piezometric surface considered, only E is taken from a part of the area underlain by the Ocala limestone in which some unusual condition does not exist, and even this profile shows a gradient considerably higher than the present average for most of the area.

The statement is made that the 40-foot contour " will lie south of the point *C* in the vicinity of Lake Weir " (p. 568), but there is no statement as to the position of the 50-foot contour, which is now north of Lake Weir, as shown on Stringfield's map, or the 60-foot or higher contours.

At present, the flow of the ground water from a large area in Sumter County, as shown by the contours in Fig. 8, is almost due west, past the Withlacoochee River and Lake Tsala Apopka, to the Gulf of Mexico. Following construction of the canal, the water level obviously will drop considerably in a large part of this area. Paige recognizes this prospective drop when he relocates the 40-foot contour between Lake Weir and the point where it crosses the Withlacoochee River near the boundary between Hernando and Sumter counties (p. 568). However, he does not discuss the effects of such a drop on Lake Tsala Apopka, the Withlacoochee River, or the ground-water level west of the river except to say that a dam will be built across the river.

Paige also assumes that the ultimate effect on the ground-water level " may be regarded as equivalent to revolving the area *ABC* on the axis *A–B* with the points *A* and *B* fixed in space, and the point *C* lowered 40 feet " (p. 567). The logical conclusion from this postulate would be that the water level would be lowered more or less throughout the entire triangular area, as far back as the point *A*. However, no such geometrical solution of this hydrologic problem is possible. Moreover, the assumptions that the point *A* will remain fixed in space and that the terrain along the line *A–B* will be unaffected appear to be merely begging the

question. Theoretically the reduction in water level along the canal would extend, with full value, to point *A* except as counteracting influences would be concomitantly introduced, such as increased intake from the surface, diversion to the canal of ground water that normally flows in other directions, and decreased cross-section area near the canal resulting from lowering of the water table and rise of the salt-water contact. The exact quantitative effects of these mitigating influences can not be determined with the data at present available. It certainly seems therefore that Paige's rather specific postulate that "after the canal is dug and the water table is adjusted, the 40-foot contour will lie south of the point *C* in the vicinity of Lake Weir and curve off to the southwest to meet the present position of this contour where it crosses the Withlacoochee River" (p. 568), implies an abundance of data that apparently does not exist and an ease of interpretation that we do not believe is possible.

Effects on Ground-water Levels North of the Canal.

The paper under consideration gives little about the piezometric surface north of the canal. The discussion of the effects of the canal on water-table slopes (pp. 565–568) deals only with the area south of the canal, although Silver Springs, Blue Springs, and other important features that may be affected are on the north side. It should be apparent that the drop in the piezometric surface may conceivably extend a considerable distance toward the north, over a wide area. If, according to the reasoning on pages 565 to 568, the 40-foot contour of the new piezometric surface south of the canal would be near Lake Weir, which is about 10 miles from the canal, the corresponding contour north of the canal might be expected to lie about as far away. If the gradient should be more nearly that of profile *E*, the effect would extend farther. Consequently, there should be a marked effect on these springs, especially on Silver Springs, which is only about 3 miles from the canal route and has an altitude of about 40 feet.

Although lowering of the piezometric surface and consequent diminution in flow seem inevitable under the conditions postulated

by Paige, he makes the categorical statement that " neither Silver Springs nor Blue Springs will be injured " (p. 569). He states that dams are to be constructed across Silver Springs Run and Blue Springs Run and across the Withlacoochee and Oklawaha Rivers which will maintain the water-table elevation, and he notes for comparison the effectiveness of the Inglis dam of the Florida Power Corporation on the Withlacoochee River. However, the contours of the piezometric surface in the vicinity of the Inglis dam show without doubt that there is great leakage around the dam. Furthermore, the conditions at the Inglis dam are not entirely comparable with those at Silver Springs and Blue Springs. At Inglis a dam across an open channel forces the water to find a route through the surrounding rocks; in contrast, the canal would provide the ground water with routes of escape through a long stretch at a lower level. The proposed dams across the mouths of Silver Springs Run and Blue Springs Run may be compared to an unfinished dam which has been built in the middle of a stream but does not extend to the banks, leaving the water to flow around its ends. It is difficult to conceive of dams across the mouths of these streams being effective in maintaining the flow of the springs, unless perhaps the bottom and sides of the canal were effectively grouted and the solution cavities were walled up for stretches of at least several miles. His statement that " neither Silver Springs nor Blue Springs will be injured " seems to us to be contrary to accepted hydrologic principles as interpreted in the light of geologic knowledge of this part of Florida.

Salt-water Conditions.

The principles of the relation between fresh ground water and the salt water of the ocean are well known as the result of the work of Badon Ghyben, Herzberg, and other European hydrologists, and have been introduced into the hydrologic investigations in this country through the work of W. E. Spear [16] and John

[16] Spear, W. E.: Long Island sources—additional supply of water for the City of New York, vol. 1, pp. 149–151, 1912.

S. Brown.[17] Paige's statement of these relations is, in general, correct (pp. 547–548). His paper shows Stringfield's maps of the area of artesian flow (Fig. 3, p. 544) and of the piezometric surface of the artesian water (Fig. 8, p. 552), but he makes no reference to the map[18] of the area in which ground water with a chloride content of more than 100 parts per million is present at moderate depths. On the northwest this area begins in Dixie County, near the mouth of the Suwannee River. It extends as a narrow band southward along the Gulf Coast and around Tampa Bay. South of Tampa it widens somewhat, and near Sarasota its landward boundary turns east around the north end of Lake Okeechobee. Along the Atlantic Coast the area extends much farther inland and ranges in width from about 20 miles in part of Brevard County to about 40 miles in Volusia County. The boundary lies west of the St. Johns River from the source of the river in Brevard County to the northeastern part of Putnam County, where it crosses the river, and reaches the ocean near St. Augustine. Within a short distance north of St. Augustine water high in chloride has not been found even in deep wells.[19] Two "islands" in which water low in chloride is present occur within the area high in chloride where this area is widest along the eastern side of the peninsula.

It is noteworthy that the greatest inland extension of the area of chloride water on the east side is east of the saddle of the piezometric surface, that is, where the contours of that surface bend far inland; also, that the northern of the two "islands" of fresh water is in the general locality of a "peninsula" of relatively high artesian head on Stringfield's contour map and the other is in a corresponding "island" of relatively high artesian

[17] Brown, J. S.: Relation of sea water to ground water along sea coasts. Am. Jour. Sci., 5th ser., vol. 4, pp. 274–294, 1922; A study of coastal ground water. U. S. Geol. Surv. Water-Supply Paper 537, pp. 16–17, 1925.

[18] Water-Supply Paper 773–C, pl. 16.

[19] Collins, W. D., and Howard C. S.: Chemical character of waters of Florida. U. S. Geol. Surv. Water-Supply Paper 596, 1928; see wells at Mayport, Duval County (p. 213), and St. Augustine, St. Johns County (p. 227). The Geological Survey has also many unpublished field tests of chloride content.

pressure.[20] From these facts the conclusion seems justified that there is a definite relation between the artesian head and the presence or absence of mineralized water. In certain places some of the salt water is doubtless connate water, water that entered the formations during a higher stand of the sea, or water of other origin, but in general the relations between fresh water and salt water are those to be expected according to the theory of Badon Ghyben and Herzberg.

Paige states (p. 549) that "along the Florida Coast from Tampa to Palm Beach . . . the Ocala limestone outcrops on the continental shelf at such great depths that the existing fresh water heads in the hinterland are insufficient to produce flow into the sea"; and that "the surplus water that does not escape at the surface is forced to travel in northeasterly and northwesterly directions to escape along the Gulf Coast north of Tampa and along the Atlantic Coast north of Palm Beach, where the Ocala outcrops on the shelf at higher elevations. This condition prevails, as is shown by the fact that ground water on the eastern and western flanks of the southern water-table high is highly mineralized." The mechanics by which the water is "forced" to move northward is not explained and is certainly not self evident. The theory seems to be in contradiction to the concept that contours of a piezometric surface show the hydraulic gradient and the direction in which the water flows, for it would require the mineralized water to move long distances parallel to the contours or even up the slope of the piezometric surface. Thus, in moving from the vicinity of Palm Beach to the area along the Atlantic coast north of latitude 28°, it would be necessary for the mineralized water to cross a divide in the piezometric surface at about that latitude. Likewise, the contours of the piezometric surface in the vicinity of Sarasota and in a much longer stretch along the Gulf show a definite hydraulic gradient toward the Gulf coast, indicating flow into the Gulf or toward the Gulf with upward leakage but not northward coastwise movement.

[20] Stringfield, V. T.: Artesian water in the Florida peninsula. U. S. Geol. Surv. Water-Supply Paper 773–C, pp. 152, 163, and pls. 12, 16, 1936.

Paige attempts to use this assumed northward movement of water to explain the highly mineralized ground water on the east and west flanks of the "southern water-table high." As a matter of fact, a comparison of the quality of water in these different areas does not support the theory. For example, one of the most striking features of the chemical composition of water from some of the wells on the coast in Sarasota County [21] is the excess of sulphate over the bicarbonate and chloride. Farther north along the coast, as in Pinellas County, the water from wells does not show this excess of sulphate.[22] Water resembling sea water in composition but more than twice as concentrated was yielded by a well only 398 feet deep on the coast of Manatee County.[23] Yet wells along the coast to the north and south do not yield such water. It seems that if a northward movement of water occurred, highly mineralized water such as that found in Sarasota and Manatee Counties would be found at other places farther north along the coast.

According to the theory of Badon Ghyben and Herzberg, if the water table or artesian head of the main water body of the peninsula declines, salt water will rise beneath it. This rise should be approximately 40 feet for every foot of drop in the fresh-water head. In the part of the canal that traverses the Ocala limestone the water table along the canal will be lowered to within a few feet of sea level and therefore the salt water should theoretically come relatively near to the surface. At points farther from the canal, where the water table would stand at higher altitudes, the salt water would be held at greater depths. Thus, if the piezometric surface at Ocala had a gradient similar to that shown by Profile *E* of Fig. 11, namely about 2.1 feet per mile, the fresh-water head at Ocala would be about 10 feet with reference to sea level. This would hold the salt water at a depth of about 400 feet under nonpumping conditions. However, when

[21] Stringfield, V. T.: Florida Geol. Surv. 23d–24th Ann. Repts., pp. 166 and table 2, 1933.

[22] Collins, W. D., and Howard, C. S.: *Op. cit.*, p. 224.

[23] Stringfield, V. T.: Florida Geol. Surv. 23d–24th Ann. Repts., p. 219, 1933.

the head would be reduced by pumping of wells the salt water would rise in a cone-shaped body and might enter the wells.[24]

The most serious effects of salt-water encroachment may occur at considerable distances from the canal, along the present margin of the area of highly mineralized water, where there is now a delicate balance between the fresh and salt water.

Effects on the Water Supply of the Sanford District.

In the vicinity of Sanford, in Seminole County, a large quantity of water from the Ocala limestone is used to irrigate celery and other truck crops, which in some years have a value running into millions of dollars. Paige mentions only the water supply of the city of Sanford. He admits that "the wells at Sanford are already affected by bottom-water salting" but asserts that "the canal-cut will have no appreciable effect on the water supply of Sanford" because the wells "cannot be affected except by a reduction of the water table in the southern high, which is not to be expected from the construction of the canal" (p. 570).

For the reasons stated above, we believe that construction of the canal would cause a considerable drop in the artesian head where the Ocala limestone is under confining beds east and southeast of Silver Springs. Probably a considerable part of the territory in which the artesian water is now tributary to the area of artesian leakage around Lake George would become tributary to the canal near Silver Springs. Furthermore, if there is any significant reduction in head along the slope from the southern high of the piezometric surface it is to be expected that there will also be some reduction in head on the east flank. This would permit a rise of salt water, which would not make much difference in localities where the water is already too highly mineralized for

[24] The effects of pumping in producing salt water contamination are shown by Stringfield, V. T.: Ground-water resources of Sarasota County. Florida Geol. Surv. 23d–24th Ann. Repts., figs. 20 and 21, 1933; Barksdale, H. C., Sundstrom, R. W., and Brunstein, M. S.: Supplementary report on the ground-water supplies of the Atlantic City region. N. J. State Water Policy Comm. Special Rept. 6, figs. 5 and 6, 1936.

use, but which might be crucial in border-line areas such as the Sanford district. The water in part of this district now has a mineral content that is near the limit for use, and a comparatively small increase in mineralization would put a large part of this thriving district out of business. A reduction in artesian head of only 1 foot at Sanford, which would permit the salt water to rise about 40 feet, might be sufficient to produce this adverse condition. Furthermore, most of the wells now flow, and irrigation is accomplished without pumping. But the water in many of the wells rises only a few feet above the surface, and a small reduction in head would cause such wells to cease flowing. We believe that such results are distinct possibilities and that they deserve serious consideration instead of being swept aside under the assumption that no damage will be done.

D. G. THOMPSON, O. E. MEINZER AND V. T. STRINGFIELD.

U. S. GEOLOGICAL SURVEY,
WASHINGTON, D. C.,
July 2, 1937.

BLOCK DIAGRAMS.

Sir.—A paper by Dr. L. U. DeSitter [1] which should have been reviewed in our recent summary of the methods of constructing block diagrams [2] has just come to our attention.

DeSitter describes a precision instrument built in the Kamerlingh-Onnes Laboratory of Leyden that embodies the linkage of Van der Hoop. By means of an adjustable stylus and pencil the angle of view of the block diagram can be varied between 0° and about 26°. For higher angles of view, including the common isometric projection with an angle of view of 35° 15′+, considerable readjustment of the position of stylus and pencil is necessary, readjustments for which the present model of the

[1] DeSitter, L. U.: Instrument for the mechanical construction of block diagrams. Leidsche Geologische Medeelingen, vol. 8, pp. 315–324, Leiden, 1937.

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DeSitter instrument does not provide. As the device now stands it is well adapted for making block diagrams with a low angle of view but the Wentworth and Wilson instruments, which incorporate the Peaucellier linkage, are better suited for isometric drawings.

W. D. JOHNSTON, JR., AND T. B. NOLAN.

U. S. GEOLOGICAL SURVEY,
WASHINGTON, D. C.,
Oct. 11, 1937.

KALGOORLIE GEOLOGY RE-INTERPRETED.

Sir: The paper by J. K. Gustafson and F. S. Miller,[1] on Kalgoorlie geology is one of great interest to those acquainted with the field. It contains more than the title indicates, and some important new observations are put forward in the first part of the paper. Particularly is this the case with the structural features of the Older Greenstone and sediments which are presented as part of a folded series forming a flat, south pitching syncline. There are, however, a few comments which it seems desirable to offer.

First, no reasons are given as to why the Older Greenstone should be regarded as lavas of intermediate composition. The analyses quoted by Feldtmann in Bulletin 69 of the W. A. Geological Survey, indicate that the lavas were originally of basaltic composition.

The authors' geological map contains much new information at the North End of the field, and the porphyry-slate mass at the South End, which had been portrayed only as a composite unit, has been subdivided into slate and porphyry. The amount of generalization involved in the subdivision is not clear, although the effect of generalizing is evident in the interpretation of the slate in the " Boulder Dyke " as a single sheet.

The opinion is advanced that the Younger Greenstone is a sill or laccolith to conform with the mapping at the North End and with the folded contact of Younger Greenstone and Older Green-

[1] ECON. GEOL., vol. 32, pp. 285–317, 1937.

stone on the eastern side of the field. Discordances with this view are attributed to " differential response to compressive stresses and shearing." Apart from the statement that the epidiorite is obviously a moderately shallow seated intrusive, a reader might be justified in thinking that the authors' arguments would also conform to the interpretation of the Younger Greenstone as a lava flow. On the other hand, neither the sill, laccolith, nor lava hypothesis conforms with a new observation by K. J. Finucane (personal communication) at the 180 ft. level of the Imperial mine, where the east limb of an anticlinal fold in the slates is truncated by the Younger Greenstone without any sign of a fault. The slates in the Imperial mine are regarded by the authors as definitely involved in the major folding, and the contact observed by Finucane is definitely transgressive. Such an observation indicates that the Younger Greenstone cannot be entirely a sill, and further eliminates the possibility that the slate was deposited unconformably on the Younger Greenstone. It also suggests that the folding of the Older Greenstone and interbedded slates must have progressed considerably before the Younger Greenstones were intruded.

In dealing with the different lode systems, the authors recognize that the lodes of the Western Lode system stop abruptly where they encounter the Boulder Dyke, but the main lode shears are shown on their generalized plan (Fig. 11) to fault the Boulder Dyke. The text is not clear as to whether such faulting is a fact or only a suggestion. The idea, however, is not new, and was put forward years ago by Maclaren. It led to a programme of fruitless diamond drilling from the bottom level of the Ivanhoe mine in search of the Ivanhoe East lode after its supposed emergence in depth on the eastern side of the Boulder Dike. If the Boulder lode and the Ivanhoe East lode occupy fault planes, one would expect that in view of the acute angle between these lodes and the Boulder Dyke, any possible movement would be dissipated along one of the numerous slate bars that would be encountered in crossing the Boulder Dyke.

The branching tongues of the Boulder Dyke, which the

authors consider may be explained by this faulting, are comparatively long, thin, tapering masses which have been so intensely altered by the mineral solutions that their identity escaped notice for many years. It is recognized by the authors that the fracture pattern was initiated prior to the dike intrusions, and it is not unlikely that a dike, which is approximately parallel to one direction of the fracture pattern, should send offshoots along the other direction of the pattern. The bend in the Boulder Dyke itself is practically a change from one direction of the fracture pattern to the other, though it is regarded by the authors as evidence of the bending of the axial plane of the Kalgoorlie syncline.

In discussing the relation of the major rock structures to the lodes, the authors have introduced the idea that a cover of slates over the present erosion surface may have served as an impenetrable capping, and localized the ore shoots beneath, and that the falling off in grade and quantity of ore with depth may be partly due to the increasing distance from the contact. The idea, however, is not consistent with the fact that exploration at the south end, near the upper slate contact, has not disclosed any appreciably large deposits of high grade ore, whereas numerous instances of high grade ore bodies could be cited near the Younger Greenstone-Older Greenstone, or lower contact.

The claim that the Oroya shoot is to be regarded as a freak without parallel among other ore bodies in the district is an exaggeration arising from over-emphasis on its structural features. The Oroya shoot is distinctive as a gently pitching ore pipe in contrast with the vertical ore pipes in the Kalgurli and Boulder Perseverance mines. It is also distinctive as occurring in the Older Greenstone, adjacent to the Younger Greenstone contact, on the eastern limb of a south pitching minor fold whose pitch approximates to that of the ore pipe. Yet it was characterized like other ore bodies in Kalgoorlie by the occurrence of rich tellurides, and there is a broad comparison with the Boulder lode which is comparable in richness notwithstanding the fact that the Boulder lode is to the Oroya shoot like a sheet to a pencil. The Oroya shoot in its upper reaches is situated vertically above the

tip of a large dike, 100 feet wide, which is so intensely altered by the mineral solutions that its identity escaped recognition up to the time of my investigation. The upper reaches of the Boulder lode likewise occur vertically above a highly altered tongue of dike, but in depth it enters the main body of the dike and loses its values. The lower reaches of the Oroya shoot may also be said to enter a large mass of dike where it finally loses its values; at least such cannot be denied on the available information. Workings along the line of the Oroya shoot on the 1200 ft. level of the Associated mine, are in a mass of highly altered rock whose identity as altered dike or altered Older Greenstone could not be established at the time. This and similar difficulties in the mapping of the dikes through the altered Older Greenstones led to the retention of the term " calc schist " for a composite mass of Older Greenstone and dike. Such problems do not appear to have been solved by the authors.

The large dike below the Oroya shoot is exposed on the 550 ft. level of the Associated Northern, about 200 feet vertically below the Oroya shoot. The top of the dike has not been observed, but its only possible upward continuations are one or two small discontinuous dikes about 1 foot wide. The upward movement of the dike magma has therefore encountered a very marked constriction, which may be associated with its interception of the relatively flat contact of the fine-grained Older Greenstone with the massive, jointed Younger Greenstone. Such a constriction has some analogy with the imaginative and theoretical cupolas in a magma reservoir, in which the volatile constituents of the magma are capable of collecting. The analogy is strengthened by the presence of intense hydrothermal alteration of both dike and fine-grained greenstone.

A constriction of this type in a dike channel at the contact of the Older Greenstone and the Younger Greenstone is not unique at Kalgoorlie. In the bottom level of the South Kalgurli mine an albite porphyry dike is 90 feet wide in the Older Greenstone, and rapidly tapers off to a very narrow width after crossing the contact with the quartz dolerite greenstone. Hydrothermal al-

teration of the quartz dolerite greenstone is not so intense as in the Older Greenstones, but it is situated two to three hundred feet vertically below the bonanza of the South Kalgurli mine.

The source of the ore bearing solutions has been attributed by the authors to an underlying granite batholith from which the porphyry dikes also issued. The differentiation processes in the magma reservoir which led to the formation of the dike magma, I regard as a prelude to the formation and introduction of the auriferous solutions. The common association of porphyry dikes and ore bodies, not only in Kalgoorlie but throughout Western Australia, suggests that the association is not purely structural, but has a genetic significance.

F. L. STILLWELL.

UNIVERSITY OF MELBOURNE,
Nov. 18, 1937.

REVIEWS

Das Magma und Seine Produkte, I Teil: Physikalisch-Chemische Grundlagen. By PAUL NIGGLI. Pp. 379. Akademische Verlagsgesellschaft M.B.H., Leipzig, 1937. Price R. M. 34.

This book is the first volume of a two volume expanded second edition of Niggli's "Die leichtflüchtigen Bestandteile im Magma" that was published in 1920. The demand for this masterly treatise was so great that it was soon exhausted. It was followed in a few years by a work of more restricted scope dealing with magmatic processes in ore genesis in which more emphasis was laid on the geologic aspects and less on the physical-chemistry of the processes. It was translated into English in 1929 by H. C. Boydell with the title "Ore Deposits of Magmatic Origin: Their Genesis and Natural Classification." The present work covers a wider field than the original. Its scope is the entire magma and is not centered on the "easily volatile constituents." The first volume has the title "Physikalisch-Chemische Grundlagen" (Physical-Chemical Principles), the second will have the title "Magmatische Gesteine und Minerallagerstätten" (Magmatic Rocks and Mineral Deposits). In other words, the first volume concerns itself with the physical-chemical laws governing the magma, and the second volume will deal with the products that result.

The problems presented by the magma are among the most difficult that confront the geologist. The geologic field of observation is limited to a small part of the whole. As Niggli points out, the geologic view never reaches to the equivalent of the order of 100 Km into the interior of the earth, and yet 100 Km is less than 3 percent of the earth's radius. The view of the processes in action is still more restricted and limited to volcanic activity. The task of the geologist is to extrapolate to a description and understanding of the whole. The goal is even theoretically attainable only to the extent to which the physicist and the chemist have made known the principles controlling the behavior of a system as complex as the magma. The master must be physicist, chemist, and geologist. The author of this work has come as near to achieving such versatility as any one, and has established an authoritative reputation as a student of the magma. A comprehensive presentation of the state of our under-

standing of the magma by him marks an outstanding advance in geologic science.

The introduction first differentiates between the magma and magmatic processes and other geologic processes and their products, and defines the constituents of the magma physico-chemically. Rock magmas are defined as molten molecular solutions belonging to or coming from the interior of the earth and constituting geologic entities. Unknown is whether a magma was always liquid or if it was at an earlier time a rock. The loose and confused usage of the term migmatite is objected to. The term migmatic should be restricted to products that lie between those formed solely from magma and those formed by metamorphism. In the latter process the major part of the mass is never in the liquid state, though it may be ultimately completely transformed by solutions and vapors. If at some stage of its transformation at least half of the geologic entity was in the liquid phase and the portion in the solid phase was in the nature of a relict and not the product of early crystallization, then the process might rightly be termed migmatic.

The magma contains two sharply differentiated groups of constituents —the difficultly volatile and the easily volatile. The former consist of constituents with melting points up to 1000° to 3000° C. and which as melts possess inappreciable vapor pressures. They are the extremely refractory substances. To them belong most of the oxides, aluminates, and silicates. The latter are constituents that at ordinary temperature and pressure are in the gas phase or which have boiling points and critical points far below the melting points of the first group. Examples are halogen compounds and water. Between these two groups are intermediate substances that yield a gas phase at atmospheric pressure below 1000° C., such as carbonates and hydrous silicates, or which volatilize under conditions under which the first group still shows a negligible vapor pressure.

The second part of the introduction is an historical account of views concerning the rôle of the readily volatile substances from the Middle Ages to the middle of the 19th century. Understanding of magmatic processes was limited by the stage of progress in related sciences. Failure to differentiate between heat and fire retarded that understanding. Later it was recognized that magmas had a fluidity far greater than their temperature alone could account for and the presence of fluxing media was postulated. This led to speculations concerning the nature of the fluxing media and how they became part of the magma. That a relation existed between laboratory experimentation and natural phenomena was recognized toward the end of the 18th century. Progress was delayed for a while by the quarrel between the Vulcanists and the Neptunists, and it was not until the middle of the 19th century that the rôle of volatiles

in deep seated igneous rocks came to the fore again. In the application of physical-chemical principles and experimentation, divergent views were developed because of slow appreciation of the fact that they pointed out only the way that nature would take under certain conditions and not necessarily the way it had taken in a given case. Conversely, the introduction closes with the admonition that today every intuitive field hypothesis must be tested in the study with the facts of physical chemistry, and must be abandoned if it does not stand that test.

This first volume is concerned with the single theme "The Physical-chemical Bases of the Study of Magmatic Systems." The mode of treatment is advanced. Niggli frankly states it is not a textbook for beginners, but the treatment presupposes a knowledge of the fundamental principles of physical chemistry and a familiarity with the literature applying them to mineralogic and petrographic problems. The development of the theme requires the coordination and blending of two opposite viewpoints and methods of work. The chemist and physicist is the analyst of nature. He seeks to dismember its complex phenomena into constituent parts that permit of a simple explanation. The mineralogist and the geologist seek to understand the whole from knowledge of a part. The geologist's advance is limited by that of the physicist and chemist. At the same time, the geologist must recognize the problems and apply the results. The chemist has studied crystallization, solution, and equilibrium mainly in dilute aqueous solutions at ordinary pressure and at temperatures not over 100° C. At high temperatures, melting and freezing has been investigated primarily in metallurgical problems. Investigations of distillation and critical phenomena have been carried out mainly with organic substances. The magma is so complex a system that its components exhibit all of these phenomena. The formation of mineral deposits from magma systems represents the separation of new phases. This in turn is a function of the number and nature of the components. The principal oxides of the magma number 9. To these must be added the subordinate and especially the easily volatile components. A proper question is how much can investigations of simple systems aid in the interpretation of so complex a system. Fortunately, conditions can be imposed upon complex systems under which they can be analyzed as simpler systems. They can be simplified by grouping chemically related and coexisting phases. A knowledge of the principles governing such analysis permits the mineralogist and petrographer to unravel the complexities of nature's processes.

Since the unraveling of these systems and the principles governing them requires their objective presentation in diagrams, a section of the book is devoted to a mathematical discussion of four necessary types of diagrams,—the pressure-temperature, the temperature-concentration, the pressure-concentration, and the pressure-temperature-concentration.

The simplest systems are those comprising solely difficultly volatile constituents. They fall into two groups—those in which the crystalline phases are of invariable composition and those in which the crystalline phases are of variable composition depending on the concentration and the physical conditions. For each group are discussed the liquid curve, which includes eutectic and peritectic points, the succession of crystallization which includes either stable or unstable phases, the relation of the field of the end crystallization phases to the original composition of the liquid, and reactions between solid phases during cooling after complete consolidation. The relations in the second group are complicated by the phenomena of solid solutions and mix crystals, reaction changes in the mix crystals, remelting of solid phases, and unmixing or exsolution. In addition to the static conditions governing the behavior of such systems, the dynamic conditions must be taken into consideration, particularly with respect to the texture and structure of the products. They determine such features as grain size, inclusions, symplectic, syantectic, keliphytic, myrmekitic, eutectic and other structures and textures. Attention is called to the fact that many of these features may originate in more than one way.

No matter how complete our understanding of the phenomena of systems comprising only difficultly volatile components may be, it can give only an incomplete understanding of magmatic processes. The temperature of complete consolidation of such systems hardly extends below 1000° C. and the melts themselves are quite viscous. Geologic observations demonstrate that magma systems that give rise to normal igneous rocks are liquid at temperatures of 800° to 600° C. and that rest magmas consolidate at temperatures below 500° C., that magmas often are not viscous, and that injections, pneumatolysis, ore deposition, and volcanic phenomena can not be explained in terms of a system with only difficultly volatile components. Consequently an extended discussion of heterogenous systems with considerable differences in volatility of the components follows. The consideration of such systems is the fundamental problem of the book.

In such systems temperature, pressure, and concentration are mutually interdependent; and crystallization, boiling, vaporization, and critical phenomena may be involved simultaneously. The analysis is carried forward again from the simpler to the more complex systems of this type. Such systems fall into two groups, those in which critical phenomena are confined to undersaturated solutions and those in which critical phenomena occur in saturated solutions. Both groups are broken down further into those not involving and those involving compounds and mix crystals. These systems involve phenomena as melting point lowering, hydrothermal alteration, distillation differentiation by cooling and by

reaction, palingenesis, progressive consolidations from a liquid-magmatic to a pegmatitic-pneumatolytic to a hydrothermal stage, liquid immiscibility, and metasomatism. The variables in these systems are so numerous, and our understanding of them so incomplete that "geologic thermometers" must be adopted with caution and conclusions based on gas and liquid inclusions must be accepted with much hesitation.

Effects that may be produced by the easily volatile constituents of great geologic significance are lowering of the consolidation temperature, lowering of viscosity even with decreasing temperature, enormous increase of vapor pressure with decreasing temperature, crystallization by vaporization, and lack of concordance of the end products of crystallization with the chemistry of the original system due to the escape of material. The important rôle of water as an easily volatile constituent is emphasized. The behavior of three important types of water-containing silicates is discussed—those with water of crystallization, the basic silicates containing (OH), and the so called acid silicates.

The final section deals with the kinetics of equilibrium. Reaction rates are discussed and their bearing on the degree and state of equilibrium of the phases that separate out. Included in this section is a discussion of magmatic assimilation. Its possibilities and its limitations are explained.

The book is both so advanced and so highly condensed that only the specialist is capable of complete understanding of its contents. Yet the subject is so fundamental to the mineralogist, petrographer, and economic geologist that workers in those fields can not afford to ignore the book because it is difficult reading. Fortunately numerous italicised phrases and sentences guide the superficial reader and the less specialized reader to the salient features of the work.

JOSEPH T. SINGEWALD, JR.

THE JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MARYLAND.

Geologisches Wörterbuch. By C. C. BERINGER. Pp. vii + 126, figs. 51. Ferd. Enke, Stuttgart, 1937. Price 6.9 RM.

This is a glossary, mainly of German technical terms used in geology. The terms defined include simple words, defined by non-technical simple words or by familiar synonyms, compound words either expanded by clarifying clauses or explained in detail enough to be understandable to the non-specialist, recently introduced terms that are discussed in the sense of the authors who proposed them, and the names of theories and processes that are outlined in sufficient fulness to make their meanings clear.

For familar words like "Erdbeben" and "Vulkan" there are comprehensive but short essays that cover their modern conceptions and the theories that account for them, and for unusual words, synonyms are given.

The book is a convenient little compendium for the use of those who read German.

W. S. BAYLEY.

Structural Behavior of Igneous Rocks. By ROBERT BALK. Pp. 177; pls. 24; figs. 38. Geological Society of America, 419 West 117th St., New York, 1937. Memoir 5; price $1.75.

The last score of years has witnessed a steadily growing interest in the detailed systematic study of all the megascopic structural features of igneous rocks, their interrelations and their interpretation, in large part under the stimulus, directly or indirectly, of the work of Hans Cloos. The present book appropriately carries on the title page the explanatory phrase "with special reference to interpretations by H. Cloos and collaborators." The subject is also familiarly known to many as "Granite Tectonics." The author, Robert Balk, in 1925 gave the first presentation in English of the methods and interpretations developed by Cloos, was the first to publish the results of a field study of this kind in North America, and together with Ernst Cloos and others has been one of the foremost leaders in the development of the subject in this country. Because of his familiarity with the subject, the author was requested by Dr. Frank F. Grout, chairman of the Batholith Committee of the National Research Council, to summarize the present state of knowledge in this field. A large volume of literature has accumulated during the last decade, and we are fortunate indeed to have so competent an authority to review this, to elucidate the technique of study and to select for special presentation those specific examples which are best adapted to illustrate the more important results and principles.

The whole work is such a concise presentation of data and interpretations that it is impossible in a review to do more than indicate the general subjects covered. Part I, of 41 pages, is devoted to a general discussion and description of the fundamentals of primary flow structures and primary fracture systems in igneous rocks; Part II, of 76 pages, to a description and interpretation of the significance of the structure patterns and fracture systems found in specific cases and types; Part III, of 15 pages, to a discussion of related problems, such as the bearing of recent data on the hypothesis of magma emplacement by stoping and other controversial problems; and Part IV, of 17 pages, is an excellent chapter on the application of principles, mostly on the methods of studying

and recording structural elements in the field and presenting them in publications. A final appendix, Part V, is an annotated bibliography of 76 selected papers that appeared (mostly 1935–1937) after the submission of the main manuscript.

Cloos and his collaborators find that a close relation exists between patterns of flow features and fracture systems in igneous rocks and assume that the emplacement of the magma, its megascopic structures of the magmatic stage and certain fracture systems of the solid stage, are almost wholly the product of stresses originating with magma movements. They have certainly presented a most cogent body of data for such an interpretation in a multitude of cases.

Balk notes, however, that Sander claims that metamorphic rocks show some of the same structural elements that Cloos recognizes in intrusive masses, and that as yet in no single area have both the microscopic study of rock fabrics as developed by Sander, and the megascopic structural studies as carried on by the Cloos school, been adequately applied. A problem for the future is to develop dependable criteria whereby primary gneissoid rocks that may be adequately interpreted on the basis of the hypotheses of Cloos are to be distinguished from secondary gneisses whose characters have been developed by regional horizontal orogenic stresses. A table of such criteria is given by Balk, but their application to the same specific example has in certain cases yielded different interpretations by different geologists in the past.

The book is superbly illustrated and written with exceptional clarity, and the Geological Society of America is to be congratulated for publishing in such fine form at so moderate a price such an excellent educational treatise.

The author states that the thoroughgoing structure studies of igneous rocks are likely to become of value for the solution of certain problems in economic geology, and that he had intended to include a chapter on the application of such studies to lode deposits, but that the field had not yet been properly investigated. May we hope that this book will serve as a stimulus so that more papers to remedy this gap in our knowledge will appear in Economic Geology in the future. It deserves wholehearted recommendation to the attention of economic geologists.

A. F. Buddington.

Princeton University,
Princeton, N. J.

The Colorado Delta. By Godfrey Sykes. Pp. 193; figs. 74; colored map. Amer. Geographical Soc., Spec. Pub. No. 19. Carnegie Inst. of Wash. and Amer. Geog. Soc., New York, 1937. Price $4.00.

This is another of the beautifully published geographical monographs that clearly bear the stamp of the American Geographical Society. It is a

record of a great river that carved stupendous canyons and deposited the materials alternately in closed basins and in the sea. It treats of early exploration and travel; of the developments, progress, and ultimate cessation of navigation within the delta; and the author's observations and interpretation of the physiographic developments. Special studies include: the origin and physical characteristics of the detrital load; the mode of transportation of the detritus; and the effect of vegetation, evaporation, and other factors upon the sedimentation. The chapters on Physiographic History and Stream Dynamics are particularly enlightening. Further information is added regarding the Imperial Valley. The carefully chosen, beautiful plates are instructive and informative.

The Society is to be congratulated for another fine publication to its credit.

ALAN BATEMAN.

Mittelamerika. By K. SAPPER and W. STAUB. Handbook der Regionalen Geologie. Bd. VIII, Abt. 4. CARL WINTER, Heidelberg, 1937. Pp. 160. Figs. 15. Pp. 11. Price $9.00.

This discussion of Middle America (that portion of North America between the Isthmus of Tehuantepec and Panama) follows the same lines as those followed in earlier parts of this great treatise on regional geology. It deals in succession with the morphology of the district, its stratigraphy, its geological history, descriptions of the geological and physical features of its various orographic elements, and concludes with a short account of its known mineral resources, and a chapter of six pages listing the literature on the region.

Naturally there are many lapses in the narrative and many blank spaces on the geological maps, but the little book contains a vast amount of material that cannot be found gathered in any other publication. It apparently gives all that is known of the geology of the district described.

Sands, Clays, and Minerals. Vol. 3, No. 2, Sept., 1937. Ed. A. L. CURTIS, Chatteris, Eng.

The latest issue of this progressive industrial magazine contains several papers of interest to economic geologists, namely: Mining and Mineral Resources of Kenya Colony, with a geological map, by C. S. Hitchin; Early Mining Literature, by J. E. Metcalf; Beryllium and its Alloys, by L. Sanderson; Uganda, Mineral Resources and Potentialities, by L. G. Brown; Undeveloped Mineral Resources of Cornwall, by J. H. Trounson; Bentonite and its Uses in Industry, by J. N. Wilson; and Minerals of Southern Rhodesia.

BOOKS RECEIVED.

J. D. BATEMAN.

Recursos Mineraes do Estado do Rio Grande do Sul, Brazil. P. F. DE CARVALHO. Pp. 38. Serv. Geol. E Miner., Bol. 72. Rio de Janeiro, 1937. *Petroleum, iron, tungsten, copper, gold.*

Reconhecimento Geologico Na Serie Assunguy, Brazil. P. F. DE CARVALHO AND E. A. PINTO. Serv. Geol. E Miner., Bol. 71. Rio de Janeiro, 1937.

Rio Gurupy. PEDRO DE MOURA. Pp. 66; map. Serv. Geol. E Miner., Brazil, Bol. 78. Rio de Janeiro, 1936. *Reconnaissance; large map.*

Mineral Resources of the Terrace Area, Coast District, British Columbia. E. D. KINDLE. Pp. 60; figs. 14. Can. Geol. Surv., Mem. 205, 1937. Price, 25 cts. *Deposits of gold, copper, lead, zinc, silver.*

Contributions to the Study of the Ordovician of Ontario and Quebec. A. E. WILSON, J. F. CALEY, J. C. SPROULE, AND U. J. OKULITCH. Pp. 133; figs. 4; pls. 9. Can. Geol. Surv., Mem. 202, 1936. Price, 50 cts. *Detailed sections; new species; excellent plates.*

Investigations in Ore Dressing and Metallurgy, July to December, 1935. Pp. 234. Can. Bur. Mines, no. 771, 1937.

Barium Minerals (2d Ed.). J. SIMPSON. Pp. 84. Imperial Institute, London, 1937. Price, 2/. *Summary of world occurrences.*

Recent Mineral Developments in the Copper River Region, Alaska. F. H. MOFFIT. Pp. 11. U. S. Geol. Surv., Bull. 880–B, 1937. Price, 5 cts. *Small gold deposits.*

Oil and Gas Development in Illinois in 1936. A. H. BELL. Pp. 15. Ill. Petrol., No. 29. State Geol. Surv., Urbana, 1937. *Annual summary.*

Occurrence, Properties, and Preparation of Limestone and Chalk for Whiting. H. WILSON AND K. G. SKINNER. Pp. 160; figs. 48. U. S. Bur. Mines, Bul. 395, 1937. Price, 30 cts. *Descriptions; origin; many plates.*

Geology of the Country around the Queen's Mine, Bulawayo District, Southern Rhodesia. A. M. MACGREGOR, J. C. FERGUSON, AND F. L. AMM. Pp. 175; figs. 5; pls. 19; colored map. South. Rhod. Geol. Surv., Bull. 30, Salisbury, 1937. Price, 5/6. *Petrology of igneous rocks, Karoo system, kimberlite; numerous gold deposits.*

The Canadian Mineral Industry in 1936. Pp. 78. Can. Bur. Mines, No. 786. Price, 25 cts. *Brief summary of metals, industrial minerals, and fuels.*

Analyses of Coals and other Solid Fuels—1934 to 1936. J. H. H. NICOLLS AND C. B. MOHR. Pp. 139. Can. Bur. Mines, No. 779. Price, 25 cts.

The Kaiyuh Hills, Alaska. J. B. MERTIE, JR. Pp. 33; geol. map. U. S. Geol. Surv., Bull 868–D, 1937. Price, 10 cts. *General geology; gold and silver-lead deposits.*

Geology of the Anthracite Ridge Coal District, Alaska. G. A. WARING. Pp. 57; figs. 3; pls. 5; maps 8. U. S. Geol. Surv., Bull. 861, 1936. Price, 70 cts. *Lower Jurassic to Tertiary; outcrops and drill cores of coal.*

Geophysical Abstracts 87, July-December, 1936. A. AYVAZOGLOU. Pp. 98. U. S. Geol. Surv., Bull. 887, 1937. Price, 15 cts. *Abstracts of all domestic and foreign geophysical papers.*

Asbestos. O. BOWLES. Pp. 92; figs. 10. U. S. Bur. Mines, Bull. 403, 1937. Price, 15 cts. *Informative report on all phases of foreign and domestic occurrences, physical properties, production and fabrication.*

Geology of the Piseco Lake Quadrangle, New York. R. S. CANNON. Pp. 107; figs. 17; maps 3. State Museum Bull. 312. Albany, 1937. *General geology; non-metallics.*

Geology of the Santa Clara Quadrangle, New York. A. F. BUDDINGTON. Pp. 56; figs. 6. State Museum Bull. 309. Albany, 1937. *General geology.*

Methods of Locating Salt-Water Leaks in Water Wells. P. LIVINGSTON AND W. LYNCH. Pp. 20; figs. 5; pls. 9. U. S. Geol. Surv., W–S Paper 796–A, 1937. Price, 10 cts.

Flood on Republican and Kansas Rivers, May and June, 1935. R. FOLLANSBEE AND J. B. SPIEGEL. Pp. 32; fig.; pls. 6. U. S. Geol. Surv., W–S Paper 796–B, 1937. Price, 15 cts.

Relative Value of Gypsum and Anhydrite as Additions to Portland Cement. P. S. BOLLER AND M. HALWER. Pp. 15; figs. 4. U. S. Bur. Mines, Tech. Paper 578, 1937. Price, 5 cts. *Anhydrite-gypsum mixtures are almost as effective as pure gypsum.*

Geology of the Country around Hunters Road, Gwelo District, Southern Rhodesia. A. M. MACGREGOR. Pp. 78; pls. 8; geol. map. South. Rhod. Geol. Surv., Bull. 31. Salisbury, 1937. Price, 2/3. *Gold, iron, manganese, nickel, copper, limestone, clay, and barite.*

Bibliography of Chinese Geology up to 1934. TSUN-YI YANG. Pp. 241. Nat. Acad. of Peiping, 1935. *Bibliography alphabetically arranged under authors, and subject index.*

Nonmetallic Mineral Resources of Eastern Oregon. B. N. MOORE. Pp. 180; figs. 11; pls. 12; maps 4. U. S. Geol. Surv., Bull. 875. 1937. Price, 30 cts. *Properties and geologic occurrence of asbestos, diatomite, limestone, lump pumice.*

Trabalhos Geophysicos Applicações dos Methodos Electricos. M. C. MALAMPHY et al. Pp. 49; figs. 31. Serv. Geol. E Miner., Brazil, Bol. 81. Rio de Janeiro, 1937. *Reports on field applications of electrical geophysical methods in Brazil.*

Rutilo no Brasil. S. FRÓES ABREU. Pp. 32; figs. 2; pls. 4. Inst. Nac. de Tec., Rio de Janeiro, 1936. *Occurrence and beneficiation of rutile.*

Composição Elementar E Immediata de Alguns Combustiveis Nacionaes. RUBEM ROQUETTE AND S. FRÓES ABREU. Pp. 22. Inst. Nac. de Tec., Rio de Janeiro, 1936. *Coal analysis.*

A Politica do Ouro. E PAULO DE OLIVEIRA. Pp. 46. Serv. Geol. E Mineral., Brazil. Rio de Janeiro, 1937. *Statistics of Brazilian gold production.*

Notas Geologicas, Municipio de Taquara, Rio Grande do Sul. JOÃO MIRANDA. Pp. 38; geol. map. Serv. Geol. E Mineral., Bol. 83. Rio de Janeiro, 1937. *Regional geology.*

Geologia do Municipio de Curityba. P. FRANCO DE CARVALHO. Pp. 37; pls. 21; map. Serv. Geol. E Mineral., Bol. 82. Rio de Janeiro, 1937. *Regional geology.*

Analyses of Rocks and Minerals, 1914–1936. R. C. WELLS Pp. 134. U. S. Geol. Surv., Bull. 878, 1937. Price, 15 cts. *Brings Bull. 591 up to date.*

Physical Properties of Typical American Rocks. J. H. GRIFFITH. Pp. 56. Iowa State Coll., Bull. 131. Ames, 1937. *Tests on 97 representative specimens.*

The Mineral Industry of Alaska in 1935. P. S. SMITH. Pp. 95; figs. 3; map. U. S. Geol. Surv., Bull. 880–A, 1937. Price, 20 cts. *Annual review and records of individual districts.*

Geology of the Country around Mossel Bay, Cape Province, Union of South Africa. S. H. HAUGHTON, H. F. FROMMURZE, AND D. J. L. VISSER. Pp. 48; figs. 2; pls. 3. Geol. Surv., Union of S. Africa. Pretoria, 1937. Price, 5/. *Transvaal system to late Tertiary; diamond, ochre, platinum.*

A Stratigraphical Classification and Table of Tanganyika Territory. F. B. WADE. Pp. 62. Geol. Div., Tang., Bull. No. 9. Dar es Salaam, 1937. Price, 4/–. *Descriptions, classification, and comparisons of sections and stratigraphic lexicon.*

Stratigraphic Relations of the Austin, Taylor, and Equivalent Formations in Texas. L. W. STEPHENSON. Pp. 14; fig.; pl. U. S. Geol. Surv., Prof. Paper 186–G, 1937. Price, 10 cts. *Correlation and detailed sections.*

Fossil Plants from the Stanley Shale and Jackfork Sandstone in Southeastern Oklahoma and Western Arkansas. DAVID WHITE. Pp. 24; pls. 5. U. S. Geol. Surv., Prof. Paper 186–C, 1937. Price, 10 cts. *Upper Stanley flora is later than any North American Mississippian.*

Some Deep Wells near the Atlantic Coast in Virginia and the Carolinas. W. C. MANSFIELD. Pp. 3; fig. U. S. Geol. Surv., Prof. Paper 186–I, 1937. Price, 5 cts. *Stratigraphic studies of well records indicate that the Cape Fear River region is upwarped.*

Marble Deposits of Northern Newfoundland. G. W. BAIN. Pp. 40; figs. 18; pls. 5. Nfld. Geol. Sect., Bull. 11. St. John's, 1937. *Detailed studies of all possible economic marbles.*

SCIENTIFIC NOTES AND NEWS

E. N. PENNEBAKER, chief geologist for the Consolidated Coppermines Corp., has returned to Kimberly, Nev., after having spent two months in a geological examination for the Sunshine Mining Co., at its property near Kellogg, Idaho.

DEAN A. MCGEE, Vice-President of Kerlyn Oil Company, and former chief geologist of Phillips Petroleum Company, delivered four lectures on petroleum geology on Jan. 4 to 7, 1938, to students and faculty of the University of Kansas for the Department of Geology.

RICHARD P. FISCHER is now junior geologist with the U. S. Geological Survey.

E. N. HARSHMAN has returned to Manila from Hong Kong and is now chief geologist for Minerals Research, Ltd., of Hong Kong, and geologist for Neilson & Co., Inc., in the Philippines.

OLIVER C. RALSTON, chief engineer of the nonmetals division of the U. S. Bureau of Mines, recently spent five weeks in the Western States where he investigated the phosphate fields of Idaho, Montana, Wyoming, and Utah.

The Amiranian Oil Company is extending explorations in Iran from Makran near the Arabian Sea to the edge of Russian Turkestan in the extreme north, and has the following economic geologists in the field: Frederick G. Clapp, in charge of explorations, Lester H. Thompson, Henry Hotchkiss, Frank Reeves, B. F. Buie, and Walter P. Wilson, with Dr. Hubert G. Schenck as Paleontologist.

J. A. BURGESS, formerly general superintendent of the Carson Hill Gold Mining Corp., Melones, Calif., is now general manager of the company.

WM. F. BOERICKE, formerly senior mining engineer with the Securities and Exchange Commission in Washington, has gone to the Philippines on a two-year contract as valuation engineer for the Government.

RAYMOND J. LEONARD, Dean of the Graduate College and Professor of Geology at the University of Arizona, died November 20, 1937, at Tucson, Arizona.

EMMONS MEMORIAL FELLOWSHIP.

The Emmons Memorial Fellowship in ECONOMIC GEOLOGY is available for this year (stipend $1,400). Applicants should be qualified by training and experience to investigate some problem in economic geology and should submit a definite statement of their problem to the Committee, under whose oversight the work will be undertaken at any institution approved by them. The Fellow must give his entire time to the problem, which may be used for a doctorate dissertation. Applications and accompanying testimonials should be submitted not later than March 1. Application blanks and further information may be obtained from Alan M. Bateman, Charles P. Berkey, Waldemar Lindgren, or the Secretary, Columbia University.